

*Advances in*  
**ORGANOMETALLIC  
CHEMISTRY**  
VOLUME 38



---

ACADEMIC PRESS

***Advances in***  
**ORGANOMETALLIC CHEMISTRY**

VOLUME 38

This Page Intentionally Left Blank

# ***Advances in Organometallic Chemistry***

EDITED BY

**F. G. A. STONE**

DEPARTMENT OF CHEMISTRY  
BAYLOR UNIVERSITY  
WACO, TEXAS

**ROBERT WEST**

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

VOLUME 38



**ACADEMIC PRESS**

San Diego   New York   Boston  
London   Sydney   Tokyo   Toronto

This book is printed on acid-free paper. ∞

Copyright © 1995 by ACADEMIC PRESS, INC.

All Rights Reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the publisher.

**Academic Press, Inc.**

A Division of Harcourt Brace & Company

525 B Street, Suite 1900, San Diego, California 92101-4495

*United Kingdom Edition published by*

Academic Press Limited

24-28 Oval Road, London NW1 7DX

International Standard Serial Number: 0065-3055

International Standard Book Number: 0-12-031138-0

PRINTED IN THE UNITED STATES OF AMERICA

95 96 97 98 99 00 QW 9 8 7 6 5 4 3 2 1

# Contents

CONTRIBUTORS . . . . .	vii
------------------------	-----

## Silyl Anions

KOHEI TAMAO and ATSUSHI KAWACHI

I. Introduction . . . . .	1
II. A Brief Survey of Preparative Methods . . . . .	2
III. Arylsilyl Anions . . . . .	3
IV. Alkylsilyl Anions . . . . .	11
V. Functionalized Silyl Anions . . . . .	16
VI. Polysilanyl Anions . . . . .	25
VII. Synthetic Application of Silyl Anions . . . . .	39
VIII. Theoretical Study . . . . .	45
IX. $^{29}\text{Si}$ NMR Data of Silyl Anions . . . . .	49
X. List of Silyl Anions . . . . .	49
XI. Concluding Remarks . . . . .	53
References . . . . .	53

## Not for Synthesis Only: The Reactions of Organic Halides with Metal Surfaces

JOHN S. THAYER

I. Some Basic Considerations . . . . .	59
II. Halide Adsorption on Metal Surfaces . . . . .	63
III. Mechanistic Investigations of Applied Reactions . . . . .	65
IV. Nonsynthetic Applications . . . . .	69
V. Conclusions . . . . .	74
References . . . . .	75

## The Bonding of Metal-Alkynyl Complexes

JOSEPH MANNA, KEVIN D. JOHN, and MICHAEL D. HOPKINS

I. Introduction . . . . .	79
II. Theoretical and Experimental Background . . . . .	82
III. X-Ray Crystallographic Studies . . . . .	90

IV. Vibrational Spectroscopic Studies . . . . .	120
V. Concluding Remarks . . . . .	139
VI. Appendix: Abbreviations Used in This Review . . . . .	140
References . . . . .	141

## **Organotransition-Metal Chemistry and Homogeneous Catalysis In Aqueous Solution**

**D. M. ROUNDHILL**

I. Introduction . . . . .	155
II. Metal Alkyls . . . . .	156
III. Tertiary Phosphines . . . . .	164
IV. Homogeneous Catalysis . . . . .	167
References . . . . .	184

## **Structure/Property Relationships of Polystannanes**

**LAWRENCE R. SITA**

I. Introduction . . . . .	189
II. Distannanes . . . . .	190
III. Linear Polystannanes . . . . .	205
IV. Branched Polystannanes . . . . .	215
V. Cyclopolystannanes . . . . .	217
VI. Polycyclic Polystannanes . . . . .	232
VII. Conclusion . . . . .	239
References . . . . .	240
INDEX . . . . .	245
CUMULATIVE LIST OF CONTRIBUTORS 1-36 . . . . .	255
CUMULATIVE LIST OF CONTRIBUTORS 37-38 . . . . .	259

# Contributors

*Numbers in parentheses indicate the pages on which the authors' contributions begin.*

MICHAEL D. HOPKINS (79), Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

KEVIN D. JOHN (79), Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

ATSUSHI KAWACHI (1), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

JOSEPH MANNA (79), Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

D. M. ROUNDHILL (155), Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

LAWRENCE R. SITA (189), Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

KOHEI TAMAO (1), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

JOHN S. THAYER (59), Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221



This Page Intentionally Left Blank

# Silyl Anions

KOHEI TAMAO and ATSUSHI KAWACHI

Institute for Chemical Research  
Kyoto University  
Uji, Kyoto 611, Japan

I.	Introduction . . . . .	1
II.	A Brief Survey of Preparative Methods . . . . .	2
	A. Silyllithium . . . . .	2
	B. Silylsodium and Silylpotassium . . . . .	2
	C. Silylmagnesium . . . . .	2
	D. Silylcopper and Silylcuprate . . . . .	3
	E. Silylzinc, Silylcadmium, and Silylmercury . . . . .	3
	F. Metal-Free Silyl Anions . . . . .	3
III.	Arylsilyl Anions . . . . .	3
	A. Preparation . . . . .	3
	B. Structural Study . . . . .	7
	C. Reactions . . . . .	10
IV.	Alkylsilyl Anions . . . . .	11
	A. Preparation and Reaction . . . . .	11
	B. Structural Study . . . . .	14
V.	Functionalized Silyl Anions . . . . .	16
VI.	Polysilanyl Anions . . . . .	25
	A. Preparation, Reaction, and Structure . . . . .	26
	B. Intermediates in Polysilane Syntheses . . . . .	34
VII.	Synthetic Application of Silyl Anions . . . . .	39
VIII.	Theoretical Study . . . . .	45
IX.	$^{29}\text{Si}$ NMR Data of Silyl Anions . . . . .	49
X.	List of Silyl Anions . . . . .	49
XI.	Concluding Remarks . . . . .	53
	References . . . . .	53

## I

## INTRODUCTION

The term *silyl anion* denotes the trivalent, octet, negatively charged silicon species. This chapter outlines the preparation, properties, structures, and reactions of silyl anions (1*a*–*i*). The silyl anions described here are restricted to those that contain the following counter-cations: Group 1: Li, Na, K, Rb, Cs; Group 2: Mg; Group 11: Cu; Group 12: Zn, Cd, Hg. Metal-free silyl anions, whose counter-cations are ammonium ( $\text{R}_3\text{NH}^+$  or  $\text{R}_4\text{N}^+$ ), are also described. Other silyl transition metal compounds are excluded; for these species, previous review articles should be referenced (2).

This review is intended as an overview of the literature on silyl anions

up to early 1994, so there is some overlap with previous review articles (*Ia-i*). In this article, silyl anions are formally classified in terms of structure, especially substituents on silicon. All silyl anions so far studied are compiled in Section X.

## II

### A BRIEF SURVEY OF PREPARATIVE METHODS

In this section, silyl anions are classified in terms of counter-cations, and their preparative methods are summarized.

#### A. *Silyllithium*

Silyllithiums are the most popular and most extensively investigated species among the silyl anions, and can be prepared by the following methods:

- (1) Reaction of a chlorosilane with lithium metal. This procedure forms lithium chloride as a by-product. Halogen-free silyllithiums can be obtained by procedures (2) and (3).
- (2) Cleavage of a disilane with lithium metal or alkyllithium.
- (3) Metal-lithium exchange reaction of a silyl metal compound (especially Group 12 metals) with alkyllithium or lithium metal.

#### B. *Silylsodium and Silylpotassium*

- (1) Reaction of a chlorosilane with sodium or potassium. (More severe reaction conditions are often required for silylsodium and silylpotassium than for silyllithium.)
- (2) Cleavage of a disilane with sodium or potassium alkoxide or potassium hydride.
- (3) Reaction of a disilylmercury with sodium or potassium metal.
- (4) Reaction of a hydrosilane with potassium hydride.

These species are usually more reactive than their lithium counterparts.

#### C. *Silylmagnesium*

- (1) Reaction of a silyllithium with a Grignard reagent or magnesium halide.
- (2) Cobalt-magnesium exchange reaction of a silyl-cobalt compound with a Grignard reagent.

Reaction of a chlorosilane with elemental magnesium gives rise to a disilane as a coupling product, although a silylmagnesium species is postulated as an intermediate.

#### D. *Silylcopper and Silylcuprate*

- (1) Silylcoppers and silylcuprates are obtained from reaction of silyllithiums with copper salts.
- (2) Higher order silylcuprates are obtained by transmetallation between silylstannanes and higher order alkylcuprates.

These species are useful reagents for the Si–C bond formation in organic synthesis.

#### E. *Silylzinc, Silylcadmium, and Silylmercury*

- (1) Reaction of a hydrosilane with mercury metal.
- (2) Reaction of a halosilane with diorganomercury.
- (3) Reaction of a silyllithium with the corresponding metal halides.

Bis-silyl derivatives of these Group 12 metals are readily accessible and thermally stable, and can be good precursors to the corresponding silyl–alkali metals via metal–metal exchange reaction.

#### F. *Metal-Free Silyl Anions*

In these species, the counter-cation is an ammonium salt instead of a metal. Two procedures are available:

- (1) Reaction of trichlorohydrosilane with a tertiary amine.
- (2) Cleavage of a disilane with tetrabutylammonium fluoride (TBAF).

### III

#### ARYLSILYL ANIONS

Silyl anions that have at least one aryl group on silicon are described in this section.

#### A. *Preparation*

##### 1. *Ar<sub>3</sub>SiM*

The action of Li metal on Ph<sub>3</sub>SiCl in tetrahydrofuran (THF) yields Ph<sub>3</sub>SiLi, together with LiCl as by-product (3). Ph<sub>3</sub>SiRb and Ph<sub>3</sub>SiCs are



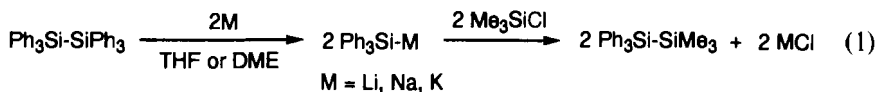
SCHEME 1

also prepared from the chlorosilane, with Rb metal and Cs metal, respectively.

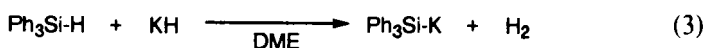
It is believed that this procedure includes three steps (Scheme 1). The first step is the initial formation of  $\text{Ph}_3\text{SiLi}$ . The resulting silyllithium reacts with the excess  $\text{Ph}_3\text{SiCl}$  to give  $\text{Ph}_3\text{SiSiPh}_3$  in the second step. The third step is the symmetrical cleavage of the disilane with lithium metal. This final step is much slower than the initial formation of silyllithium and is effected only by the electropositive alkali metals. Thus, the reaction of  $\text{Ph}_3\text{SiCl}$  with less electropositive Mg gives only  $\text{Ph}_3\text{SiSiPh}_3$ , although silylmagnesium  $\text{Ph}_3\text{SiMgCl}$  is postulated as an intermediate (4).

(*o*-Tolyl) $_3\text{SiM}$  ( $\text{M} = \text{Li}, \text{Cs}$ ) can also be prepared from (*o*-tolyl) $_3\text{SiCl}$  in the same way (3). However, it is doubtful that (*o*-tolyl) $_3\text{SiM}$  is generated via three steps like those just discussed and shown in Scheme 1, since highly crowded hexa(*o*-tolyl)disilane is hardly accessible by coupling in the second step.

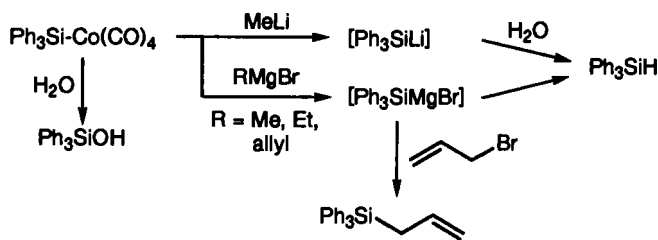
Salt-free  $\text{Ph}_3\text{SiLi}$ ,  $\text{Ph}_3\text{SiNa}$ , and  $\text{Ph}_3\text{SiK}$  are obtained by cleavage of the Si-Si bond of hexaphenyldisilane by alkali metals in ethereal solvents such as 1,2-dimethoxyethane (DME) and THF [Eq. (1)] (5,6).  $\text{Ph}_3\text{SiK}$  is



also prepared by cleavage of the Si-C bond in  $\text{Ph}_3\text{Si-CMe}_2\text{Ph}$  with Na-K alloy in ether ( $\text{Et}_2\text{O}$ ) [Eq. (2)] (7). Historically, this was essentially the first successful method for the preparation of silyl anions.  $\text{Ph}_3\text{SiK}$  may also be made by reaction of  $\text{Ph}_3\text{SiH}$  with KH at  $40^\circ\text{C}$  in DME for 6 hours [Eq. (3)] (8). This method is applicable also to the preparation of alkylsilyl anions (see Section IV-A).



A silyl-cobalt complex is a good precursor for silyllithium and silylmagnesium compounds (Scheme 2) (9a,b). Evidence for the generation of



SCHEME 2

these anionic species, especially  $\text{Ph}_3\text{SiMgBr}$ , is that hydrolysis of these species with  $\text{H}_2\text{O}$  affords only the hydrosilane  $\text{Ph}_3\text{SiH}$ , whereas hydrolysis of the silyl-cobalt complex gives the silanol  $\text{Ph}_3\text{SiOH}$  quantitatively.

In contrast to the Group 1 derivatives, Group 2 magnesium derivatives have been much less studied so far. As described earlier, the reaction of triphenylchlorosilane with magnesium metal produces the coupling product disilane. It has been found that the action of cyclohexylmagnesium bromide on  $\text{Ph}_3\text{SiCl}$  also yields  $\text{Ph}_3\text{Si-SiPh}_3$ , together with cyclohexene and cyclohexane as by-products. This finding suggests that  $\text{Ph}_3\text{SiMgBr}$  is generated in situ (10). Since  $\text{Me}_3\text{SiCl}$  does not undergo similar homocoupling by cyclohexylmagnesium bromide in refluxing THF, aromatic groups on silicon appear to be necessary for the stabilization of the silyl Grignard reagent. Reaction of  $\text{Ph}_3\text{SiLi}$  with  $\text{MgBr}_2$  also gives  $\text{Ph}_3\text{SiMgBr}$ , although the structure of this species has not been confirmed [Eq. (4)] (11) (see also Section VII).



A Group 12 derivative  $(\text{Ph}_3\text{Si})_2\text{Hg}$  is prepared by reaction of  $\text{Ph}_3\text{SiH}$  with  $(\text{PhCH}_2)_2\text{Hg}$  at 165–168°C (12).

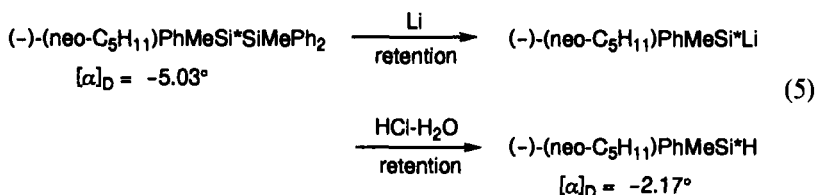
## 2. $\text{Ar}_2(\text{alkyl})\text{SiM}$ and $\text{Ar}(\text{alkyl})_2\text{SiM}$

$\text{Ar}_2(\text{alkyl})\text{SiLi}$  and  $\text{Ar}(\text{alkyl})_2\text{SiLi}$  are prepared by methods similar to those for  $\text{Ar}_3\text{SiLi}$ , that is, the action of Li metal on chlorosilanes or the cleavage of disilane with Li metal in ethereal solvent such as THF (1e). The alkyl substituents can be methyl, ethyl, *i*-propyl, *t*-butyl, benzyl, and *neo*-pentyl groups. Allyl-bearing silyllithium can also be prepared from the corresponding chlorosilane with Li metal in THF at 0°C (see Section VII) (13). Vinyl-bearing silylpotassium is obtained from the corresponding hydrosilane with KH in DME at 40°C (see Section III-A-1) (14). A copper derivative,  $\text{PhMe}_2\text{SiCu(CN)Li}$ , and a magnesium derivative,  $\text{PhMe}_2\text{SiMg}$ -

*i*-Pr, can be prepared from  $\text{PhMe}_2\text{SiLi}$  with  $\text{CuCN}$  and *i*-PrMgX (*X* = halide), respectively. Synthetic applications of these reagents are described in Section VII.

When all substituents are different, a chiral center is present on silicon. Enantiomeric silyl anions are generated in three ways, with retention of configuration; for the configurational stability of silyllithium, see Section III-B.

Optically active silyllithium (*neo*- $\text{C}_5\text{H}_{11}$ ) $\text{PhMeSi}^*\text{Li}$  is obtained by cleavage of an optically active disilane with lithium metal, with retention of configuration [Eq. (5)] (15). Formation of optically active silyllithium (1-Np) $\text{PhMeSi}^*\text{Li}$  (Np = naphthyl) and silylmagnesium reagent (1-Np) $\text{PhMeSi}^*\text{MgBr}$  is also observed in reactions of an optically active silyl-cobalt complex (9*a,b*). Treatment of the enantiomer (+)-(1-Np) $\text{PhMeSi}^*\text{Co}(\text{CO})_4$  with MeLi produces, after hydrolysis, the optically active silane (+)-(1-Np) $\text{PhMeSi}^*\text{H}$ , with 70% retention of configuration. Similarly, treatment with a Grignard reagent yields a silyl Grignard reagent of low optical activity (*cf.* Scheme 2).

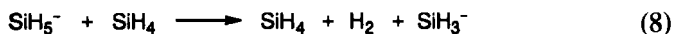
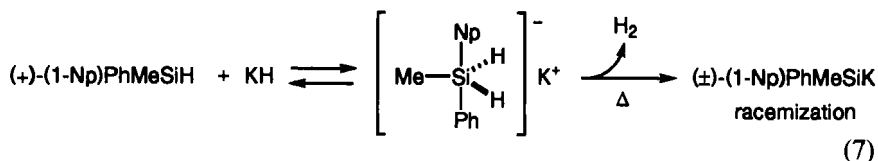


Enantiomeric silylmercury compounds are obtained from reaction of diorganomercurys with an optically active hydrosilane [Eq. (6)] (16). The configuration is retained predominantly at silicon. These compounds, however, racemized readily when sublimed during purification.



Reaction of an enantiomeric hydrosilane with KH yields a racemic silyl anion (17). Thus, treatment of (+)-(1-Np) $\text{PhMeSiH}$  with KH at 50°C in DME for 24 hours and subsequent addition of *n*-BuBr give racemic ( $\pm$ )-(1-Np) $\text{PhMeSi-}n\text{-Bu}$ , via the formation of the corresponding silyl anion with loss of optical activity. Hydrolysis or deuterolysis also gives a racemic product. These observations clearly rule out a mechanism in which the silyl anion is formed by proton abstraction from the hydrosilane, because retention of configuration would be expected. A possible mechanism involves a pentacoordinate dihydrosilyl anion formed via coordination of  $\text{H}^-$  in an initial fast, reversible process, and its decomposition to the racemic silyl anion with loss of molecular hydrogen [Eq. (7)]. A gas-

phase study supports this mechanism: Pentacoordinate silyl anion  $\text{H}_5\text{Si}^-$  decomposes to yield  $\text{H}_3\text{Si}^-$  and  $\text{H}_2$  [Eq. (8)] (18).



### B. Structural Study

$^{13}\text{C}$  nuclear magnetic resonance (NMR) studies provide much information on the electronic structure of phenylsilyl anions (19–20). The main interest is the charge delocalization of lone pair electrons from silicon to the phenyl group. The  $^{13}\text{C}$  chemical shift changes on phenyl rings on going from chlorosilanes to the corresponding silyl anions give the major trends: The ipso carbon is strongly deshielded, and the para carbon is shielded (Table I, Fig. 1) (19a). As seen in Fig. 1, the charge distribution pattern

TABLE I  
 $^{13}\text{C}$  NMR CHEMICAL SHIFTS OF SILYL ANIONS AND RELATED SPECIES IN THF (ppm)<sup>a</sup>

	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	Reference
$\text{Ph}_3\text{SiCl}$	133.8	135.9	128.9	131.5	(19a)
$\text{Ph}_2\text{MeSiCl}$	134.4	134.0	128.1	130.5	(19c)
$\text{PhMe}_2\text{SiCl}$	137.0	133.8	128.8	131.0	(19a)
$\text{Ph}_3\text{SiLi}$	155.9	137.0	126.9	124.6	(19a)
$\text{Ph}_2\text{MeSiLi}$	160.1	135.4	126.7	123.9	(19a)
$\text{PhMe}_2\text{SiLi}$	166.0	133.8	126.5	122.7	(19a)
$(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$	158.5	135.6	126.6	123.9	(19a)
$(\text{Et}_2\text{N})_2\text{PhSiLi}$	160.0	134.9	126.6	123.2	(54a)
$(\text{Et}_2\text{N})\text{PhMeSiLi}$	164.8	133.7	126.5	122.7	(54a)
$\text{Ph}_3\text{SiK}$	158.6	136.9	126.7	123.8	(19a)
$\text{Ph}_2\text{MeSiK}$	163.2	135.1	126.5	123.0	(19a)
$\text{PhMe}_2\text{SiK}$	170.1	133.6	126.4	121.6	(19a)
$(\text{PhMe}_2\text{Si})_2\text{CuLi}^b$	162.0	134.7	126.3	123.9	(99)
$\text{PhMe}_2\text{SiCu}(\text{CN})\text{Li}^b$	150.0	135.0	126.0	124.6	(99)
$(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2^b$	157.4	134.9	126.5	124.6	(99)
$\text{Me}(\text{PhMe}_2\text{Si})\text{Cu}(\text{CN})\text{Li}_2^b$	159.2	135.3	127.2	125.1	(99)

<sup>a</sup> Cyclohexane used as reference ( $\delta$  27.7).

<sup>b</sup> THF used as reference ( $\text{C}_\alpha$ ,  $\delta$  26.0;  $\text{C}_\beta$ ,  $\delta$  68.2).



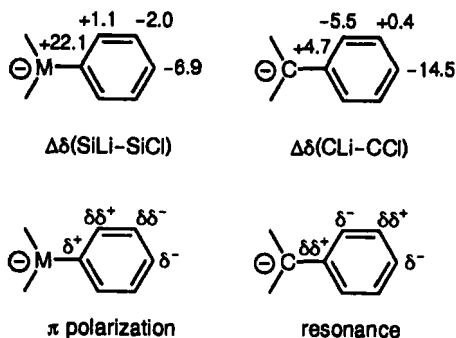


FIG. 1.  $^{13}\text{C}$  chemical shift changes (+ sign means downfield shift) on going from  $\text{Ph}_3\text{SiCl}$  to  $\text{Ph}_3\text{SiLi}$ , and schematic representations of the electron distribution. Data for the corresponding carbanion are also shown, for comparison.

is typical for a  $\pi$ -polarization effect and quite different from the pattern of a resonance effect. Thus, a large amount of negative charge remains on the silicon atom.

The ultraviolet (UV) spectra of (phenylsilyl)lithiums are consistent with these NMR studies (21). The absorption maximum of  $\text{Ph}_3\text{SiLi}$  in THF is observed at 335 nm, whereas that of  $\text{Ph}_3\text{CLi}$  is observed at 500 nm. The data for  $\text{Ph}_2\text{MeSiLi}$  and  $\text{PhMe}_2\text{SiLi}$  are similar to that of  $\text{Ph}_3\text{SiLi}$ . These findings suggest little conjugation between silicon and the phenyl group.

$^{29}\text{Si}$  NMR of (phenylsilyl)lithiums has been investigated (19b). The  $^{29}\text{Si}$  resonance of  $\text{Ph}_3\text{Si}^6\text{Li}$  resolves into a triplet due to coupling with one  $^6\text{Li}$  atom ( $I = 1$ ,  $^1J[^{29}\text{Si}, ^6\text{Li}] = 17$  Hz) in 2-methyltetrahydrofuran (MTHF) at 173 K (Fig. 2); detailed data are compiled in Table II in Section IX. This result implies a monomeric structure and partial covalent nature of the Si-Li bond. By increasing the temperature or by increasing the cation-solvating power of the solvent (THF > MTHF), the pace of the lithium-lithium exchange reaction is increased, resulting in the disappearance of the  $^{29}\text{Si}$ - $^6\text{Li}$  coupling. The exchange rate is decreased if methyl groups are substituted for phenyl, and a well-resolved triplet can be observed for  $\text{PhMe}_2\text{SiLi}$  at 173 K, even in THF (Fig. 2).

Crystal structure analysis of  $\text{Ph}_3\text{SiLi} \cdot 3\text{THF}$  has revealed that both of the lithium and silicon centers are four-coordinate with distorted tetrahedral geometries (22). The Li-Si distance is 2.67 Å and very similar to the averaged Li-Si bond length (2.68 Å) observed in  $(\text{LiSiMe}_3)_6$  (see Section IV-B). The averaged Si-C(phenyl) distances are 1.94 Å, which is much longer than that normally observed in neutral compounds (ca. 1.85 Å). The lengthening may be a consequence of the increased negative charge density on silicon, which reduces the ionic contribution to the Si-C bond

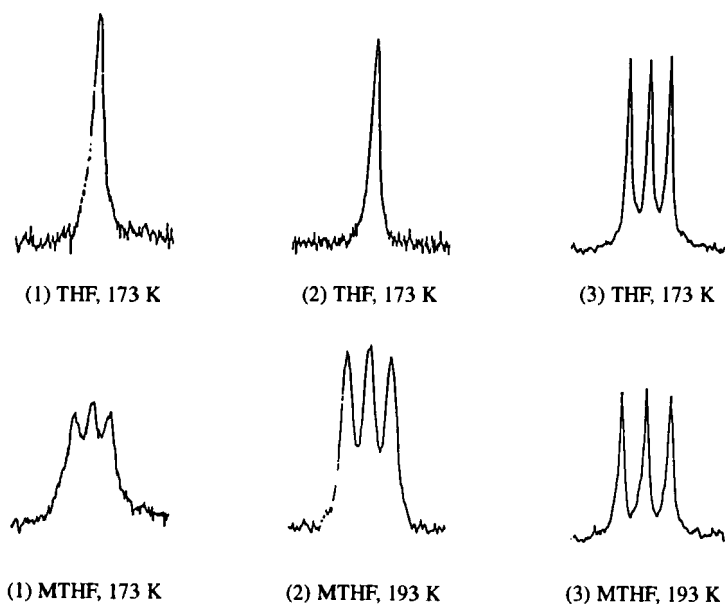
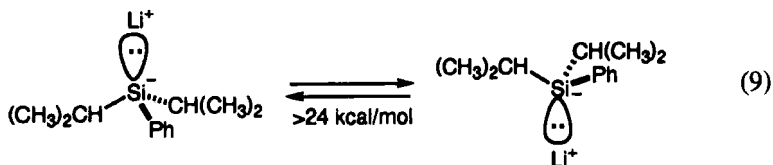


FIG. 2. Low-temperature  $^{29}\text{Si}$  NMR of  $\text{Ph}_3\text{Si}^-\text{Li}^+$  (1),  $\text{Ph}_2\text{MeSi}^-\text{Li}^+$  (2), and  $\text{PhMe}_2\text{Si}^-\text{Li}^+$  (3), 0.3 M solution in THF or MTHF (19b). Reprinted with permission from *J. Am. Chem. Soc.*, **1985**, 107, 6408. Copyright (1985) American Chemical Society.

strength. The tetrahedral geometry about the silicon is in clear contrast to the planar coordination at the central carbon of the carbon analog,  $\text{Ph}_3\text{CLi}\cdot\text{Et}_2\text{O}$  (23). This finding is consistent with the conclusion of the  $^{13}\text{C}$  NMR studies mentioned earlier.

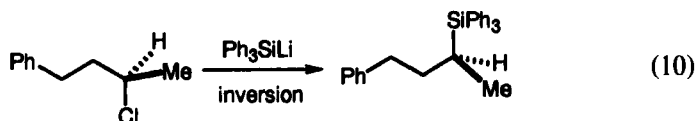
Configurational stability of  $\text{Ph}(i\text{-Pr})_2\text{SiLi}$  has been estimated by means of  $^1\text{H}$  NMR [Eq. (9)] (24). The two methyl groups in each isopropyl group are diastereotopic and anisochronous at room temperature in a wide range of solvents. The nonequivalence is observed up to  $185^\circ\text{C}$ . Since rotation around the  $\text{Si}-\text{C}$  bonds appears to be fast on the NMR time scale, the nonequivalence of the isopropyl methyl groups in the anion is evidence for slow inversion about silicon. This result indicates that unimolecular atomic inversion about silicon must be slow on the NMR time scale, and a lower limit to inversion about the trivalent silicon can be set at about 24 kcal/mol, which is consistent with theoretical studies (see Section VIII).



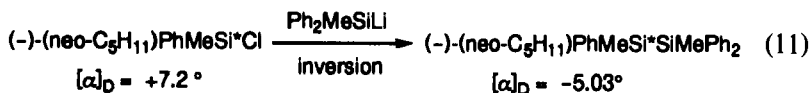
### C. Reactions

#### 1. Stereochemical Aspects

Reaction of an optically active secondary alkyl chloride with  $\text{Ph}_3\text{SiLi}$  proceeds with complete (100%) inversion of configuration. The process is a normal  $\text{S}_{\text{N}}2$  reaction [Eq. (10)] (25).

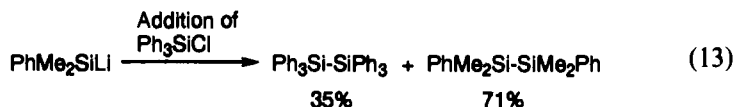
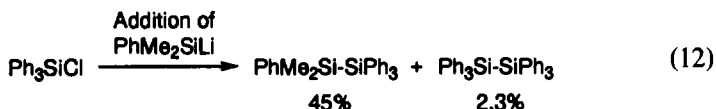


Reaction of an optically active chlorosilane with  $\text{Ph}_2\text{MeSiLi}$  proceeds with inversion of configuration to give an optically active disilane [Eq. (11)] (15).



#### 2. Reaction of Silyllithium with Chlorosilane: Halogen-metal exchange and Si-Si Bond Cleavage Reaction

It has been reported that in reactions of silyllithium with chlorosilane, the products depend on the mode of addition (26,27), as shown by the following two examples: Whereas addition of silyllithium to chlorosilane gives the desired cross-coupled disilane [Eq. (12)], addition of chlorosilane to silyllithium forms a mixture of homo-coupled disilanes [Eq. (13)].

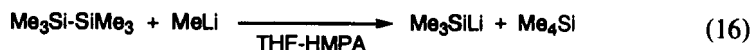


Unusual homo-coupling reactions observed in Eq. (13) have been explained in terms of (1) halogen-metal exchange and/or (2) Si-Si bond cleavage reaction. Thus, according to (1), the first step in the reaction may be a rapid halogen-metal exchange in the presence of excess amounts of silyllithium [Eq. (14)] (26). The driving force for this exchange is the generation of the more stable silyllithium  $\text{Ph}_3\text{SiLi}$ . The cross-coupling

SCHEME 3

Peralkylsilyl anions having no aromatic substituents cannot be prepared by reaction of the corresponding chlorosilane or disilane with alkali metal (except *t*-Bu<sub>3</sub>SiM). The action of alkali metals on chlorosilane gives not silyllithium but disilane as coupling product, because cleavage of the Si-Si bond of peralkyldisilane does not occur with alkali metals. The energy of the lowest unoccupied molecular orbital (LUMO) of alkyl-substituted disilanes ( $\sigma^*$  orbital of the Si-Si bond) is too high to accept an electron from the metal. At least one aryl group on silicon appears necessary for cleavage of the Si-Si bond.

Cleavage of the Si-Si bond in peralkyldisilanes by organometallic nucleophiles is successful, however.  $\text{Me}_3\text{SiLi}$  can thus be prepared from reaction of  $\text{Me}_3\text{SiSiMe}_3$  with  $\text{MeLi}$  in HMPA- $\text{Et}_2\text{O}$  (HMPA = hexamethylphosphoric triamide) [Eq. (16)] (29). This may be the only practical method for the preparation of  $\text{Me}_3\text{SiLi}$ . In a large-scale experiment, however,  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  was generated instead of  $\text{Me}_3\text{SiLi}$  (see Section VII).

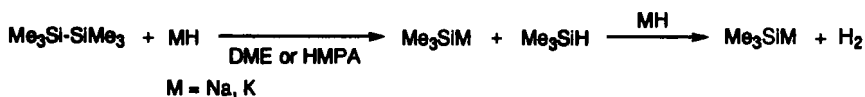
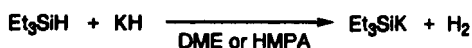


$\text{Me}_3\text{SiNa}$  and  $\text{Me}_3\text{SiK}$  are obtained from  $\text{Me}_3\text{SiSiMe}_3$  by treatment with  $\text{MeONa}$  or  $\text{MeOK}$ , together with  $\text{Me}_3\text{SiOMe}$  [Eq. (17)] (30-31). A strongly basic (coordinating) aprotic solvent such as HMPA or 1,3-dimethyl-2-imidazolidone (DMI) is essential to this reaction. The driving force for this reaction is the formation of the strong Si-O bond.



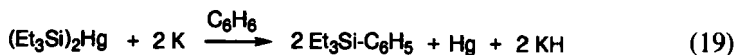
The alkali metal hydrides  $\text{NaH}$  and  $\text{KH}$  are also effective as metalating reagents for hydrosilane and disilane to give trialkylsilyl anions in an aprotic solvent such as THF, DME, or HMPA (8) (Scheme 4) (for the mechanism, see Section III-A-2). The reaction of disilane with 2 equivalents of metal hydride converts both silyl groups into silyl anions in two steps, in contrast to the reaction with  $\text{MeOM}$  described earlier.

Silylmercury compounds have long been well investigated. Some previous reviews should be referenced (*1c,d*).  $(\text{Me}_3\text{Si})_2\text{Hg}$  is prepared by reaction of  $\text{Me}_3\text{SiCl}$  in cyclopentane with  $\text{Na/Hg}$ . These reactions must be carried out in the dark to avoid photochemically induced decomposition (32). Silylmercury compounds serve as precursors for silyl-alkali metal derivatives [Eq. (18)] (33-35). Mercury-alkali metal exchange reaction proceeds in THF or benzene. Benzene gives better yields than THF, although the reaction rate is larger in THF than in benzene. If made in benzene,  $\text{Me}_3\text{SiLi}$  can be sublimed under high vacuum at  $60^\circ\text{C}$ . Reaction of a silylmercury with potassium in benzene, however, gives no  $\text{Et}_3\text{SiK}$  but instead  $\text{Et}_3\text{SiPh}$  in quantitative yield [Eq. (19)]. It is hypothesized that



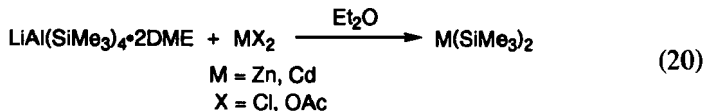
SCHEME 4

the initially formed  $\text{Et}_3\text{SiK}$  abstracts a proton from benzene to yield  $\text{Et}_3\text{SiH}$  and  $\text{PhK}$ , which couple with each other to give  $\text{Et}_3\text{SiPh}$ .

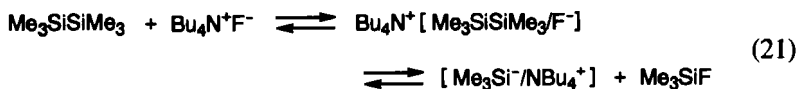


Bis(trimethylsilyl)magnesium,  $(\text{Me}_3\text{Si})_2\text{Mg}$ , can also be obtained by reaction of  $(\text{Me}_3\text{Si})_2\text{Hg}$  with magnesium metal in DME and recrystallized from cyclopentane to give pale pink crystals of  $(\text{Me}_3\text{Si})_2\text{Mg} \cdot \text{DME}$  (36).

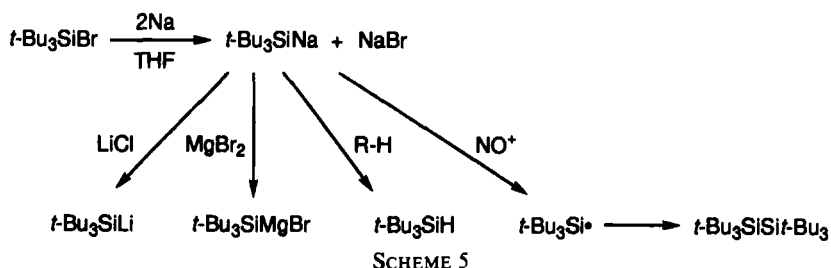
Lithium tetrakis(trimethylsilyl)aluminate,  $\text{LiAl}(\text{SiMe}_3)_4$ , prepared by reaction of  $\text{Me}_3\text{SiCl}$  with lithium and aluminum in the presence of mercury (37), reacts with  $\text{ZnCl}_2$  or  $\text{Zn}(\text{OAc})_2$  in  $\text{Et}_2\text{O}$  to give  $(\text{Me}_3\text{Si})_2\text{Zn}$  [Eq. (20)] (38a-c). The pale yellow crystalline product is isolable by vacuum sublimation and is readily soluble in ethers, benzene, or pentane. The silylzinc compound can be stored for about three weeks at  $-20^\circ\text{C}$ , but decomposes slowly, with separation of the metal, at room temperature. The cadmium analog,  $(\text{Me}_3\text{Si})_2\text{Cd}$ , is synthesized in the same way. The silylcadmium is less stable than the silylzinc and decomposes within two days, with precipitation of the metal, even at  $-20^\circ\text{C}$ . This compound is also light-sensitive.



A metal-free trimethylsilyl anion is formed from hexamethyldisilane by cleavage with TBAF in HMPA in equilibrium concentration, as revealed by  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis of the reaction mixture. Treatment of trisilane with TBAF provides  $\text{Me}_3\text{SiMe}_2\text{Si}^-/\text{NBu}_4^+$  and  $\text{Me}_3\text{SiF}$ ; the fluoride anion attacks at the terminal silicon of trisilane [Eq. (21)] (39). Synthetic application of this species is described in Section VII. Other metal-free silyl anions are described in Section V.

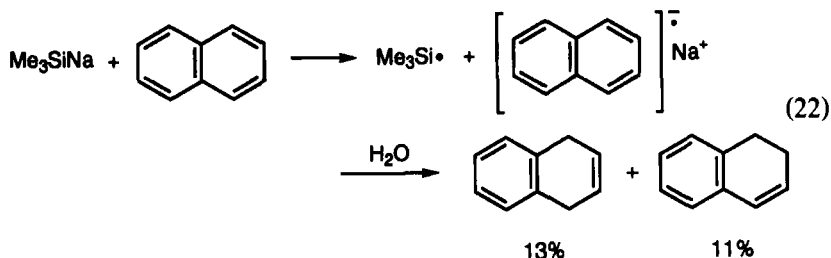


A sterically crowded silyl anion, tri-*tert*-butylsilylsodium (*t*- $\text{Bu}_3\text{SiNa}$ ), is produced from *t*- $\text{Bu}_3\text{SiBr}$  and  $\text{Na}$  in refluxing THF (Scheme 5) (40). In this reaction, the coupling product, *t*- $\text{Bu}_3\text{Si-Si-}t\text{-Bu}_3$ , is not formed, because of the high steric hindrance at silicon. The compound crystallizes as yellow needles from a solution in pentane at  $-78^\circ\text{C}$ . Its  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{23}\text{Na}$  NMR studies indicate the constitution to be *t*- $\text{Bu}_3\text{SiNa} \cdot 2\text{THF}$ .



Similarly,  $t\text{-Bu}_3\text{SiK}$  is obtained from  $t\text{-Bu}_3\text{SiI}$  and K in refluxing heptane. Whereas  $t\text{-Bu}_3\text{SiM}$  ( $M = \text{Na}, \text{K}$ ) does not couple with  $t\text{-Bu}_3\text{SiX}$  ( $X = \text{Cl}, \text{Br}$ ), the disilane  $t\text{-Bu}_3\text{SiSi}t\text{-Bu}_3$  can be obtained by coupling of the silyl radical  $t\text{-Bu}_3\text{Si}^\bullet$ , which is generated by oxidation of  $t\text{-Bu}_3\text{SiM}$  by the nitrosyl cation  $\text{NO}^+$ .  $t\text{-Bu}_3\text{Si}^-$  acts as a strong base, and at higher temperatures it reacts with THF. The cesium derivative,  $t\text{-Bu}_3\text{SiCs}$ , deprotonates even hydrocarbons.  $t\text{-Bu}_3\text{SiNa}$  can be converted into  $t\text{-Bu}_3\text{SiLi}$  and  $(t\text{-Bu}_3\text{Si})_2\text{Mg}$ , respectively, by exposure to  $\text{LiCl}$  and  $\text{MgBr}_2$ .

The high electron-donating ability of  $\text{Me}_3\text{SiNa}$  causes reduction of naphthalene [Eq. (22)] (30a).



Nucleophilic substitution of aromatic halides with trimethylsilyl anions competes with reduction. The ratio of substitution/reduction increases in the direction of  $\text{I} < \text{Br} < \text{Cl}$ , and appears relatively insensitive to the metal cations (30a,b). When an electrophile is a poorer electron acceptor, such as  $\text{Ph}_3\text{GeBr}$ , nucleophilic substitution proceeds smoothly to form the coupling product in good yield (8).

### B. Structural Study

Crystal structures of  $\text{Me}_3\text{SiLi}$  and its  $\text{N,N,N',N'}$ -tetramethylethylenediamine (TMEDA) complex have been investigated by X-ray analysis (41,42).  $\text{Me}_3\text{SiLi}$  exists as a hexamer in the solid state (Fig. 3) (41). The

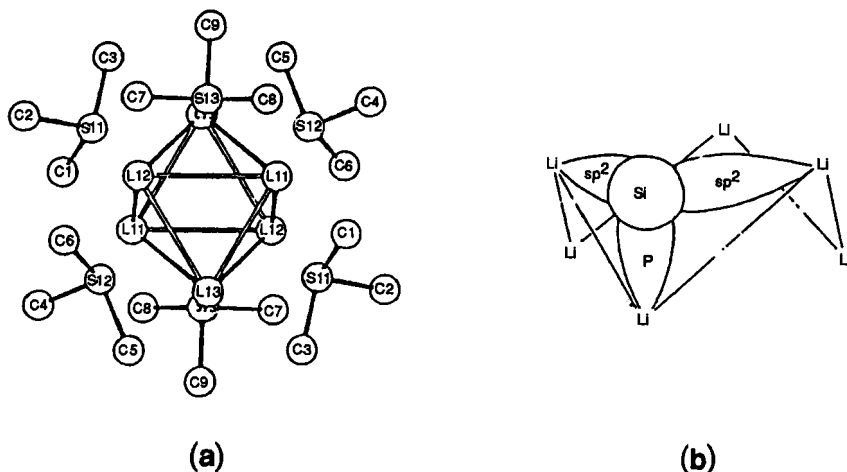


FIG. 3. (a) The  $(\text{Me}_3\text{SiLi})_6$  hexamer. (b) View of the hexamer depicting the bonding between the bridging silyl group and the lithium atoms (41). Reprinted with permission from *J. Am. Chem. Soc.* **1974**, *96*, 7593; **1980**, *102*, 3769. Copyright (1974 and 1980) American Chemical Society.

$\text{Me}_3\text{SiLi}$  framework could best be represented as a “folded chair” six-membered lithium ring of approximate  $D_{3d}$  symmetry. The  $\text{Li}_6$  chair conformation is much closer to the octahedron than to a cyclohexane structure. Each of the trimethylsilyl groups is located centrally above a triangular face in the periphery of the  $\text{Li}_6$  ring. The averaged Si–C(methyl) bond distance is 1.89 Å, which is similar to the normal Si–C single bond (1.86–1.91 Å). The averaged Si–Li distance is 2.68 Å. The bonding is explained in terms of four-centered electron-deficient Si–Li bonds with minimal Li–Li interactions. This might be viewed as the mutual coordination of two trimers with essentially  $sp^2$ -hybridized lithium atoms, leaving a  $p$  orbital available that is properly oriented to interact with the carbon or silicon atoms of the trimethylsilyl groups on the second trimeric unit to provide the necessary bonding to lead to the observed hexameric structure.

The crystal structure of  $(\text{Me}_3\text{SiLi})_2(\text{TMEDA})_3$  has also been investigated (Fig. 4) (42). The results reveal that (1) there is no Li–Si–Li bridge bonding, indicative of the complete destruction of the hexameric aggregate,  $(\text{LiSiMe}_3)_6$ , by complexation with TMEDA, and (2) the Si–Li bond distance is relatively long, 2.70 Å, compared to the averaged Si–Li distance of 2.68 Å in the uncomplexed hexamer.

Only one structural study on an Si–Mg compound has been performed. The X-ray analysis of  $(\text{Me}_3\text{Si})_2\text{Mg}\cdot\text{DME}$  (36) shows that the compound



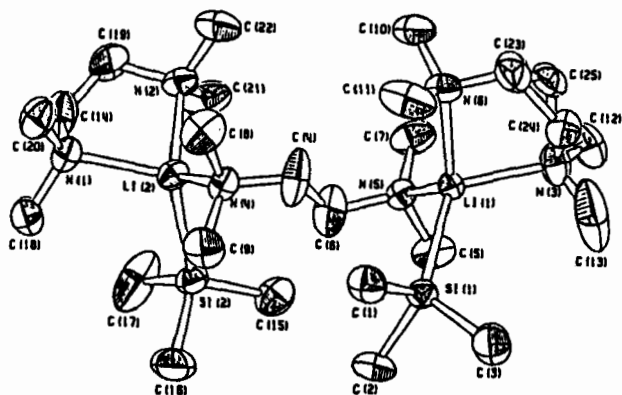


FIG. 4. An ORTEP diagram for the molecular unit  $(\text{Me}_3\text{SiLi})_2(\text{TMEDA})_3$  (42). Reprinted with permission from *Organometallics* **1982**, *1*, 875. Copyright (1982) American Chemical Society.

is monomeric in the crystal and that the magnesium atom has a distorted tetrahedron surrounded by the two silicon atoms and two oxygen atoms. The Si–Mg distance of 2.63 Å is somewhat longer than the sum of the covalent radii (2.41 Å); the averaged Si–C(methyl) distance is 1.88 Å. The Si–Mg–Si angle of 125° is greater than the tetrahedral angle, whereas the O–Mg–O angle is much smaller (76°). These angle distortions result from the steric repulsion of the bulky trimethylsilyl groups and the necessarily small O–Mg–O angle required by the bite size of the DME ligand and the Mg–O distances.

Infrared (IR) and Raman spectra of  $\text{Zn}(\text{SiMe}_3)_2$ ,  $\text{Cd}(\text{SiMe}_3)_2$ , and  $\text{Hg}(\text{SiMe}_3)_2$  indicate that these molecules are linear, because only one Si–metal stretching is observed in all cases (38a,43).

## V

### FUNCTIONALIZED SILYL ANIONS

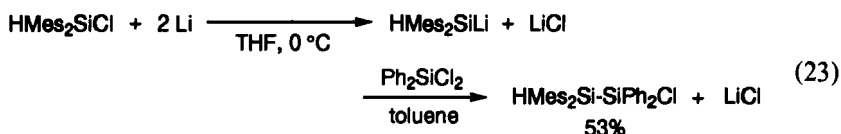
In contrast to triorganosilyl anions, functionalized silyl anions have been studied less extensively. Functional groups reported so far are hydrogen, chlorine, amino, alkoxy, and carbonyl groups. In addition to these species, silacyclopentadienide anions are also described in this section. Theoretical studies on the effect of functional groups are described in Section VIII.

### 1. Hydrosilyl Anions

Silylpotassium,  $\text{H}_3\text{SiK}$ , is obtained by the reaction of silane,  $\text{SiH}_4$ , and K in DME (44–47). The  $^{29}\text{Si}$  NMR signal in HMPA at ambient temperature is observed at  $-165.0$  ppm as a quartet ( $^1\text{J}[\text{Si}, \text{H}] = 75$  Hz) (46). The photoelectron spectra of  $\text{SiH}_3^-$  and  $\text{SiD}_3^-$  have been investigated (48).

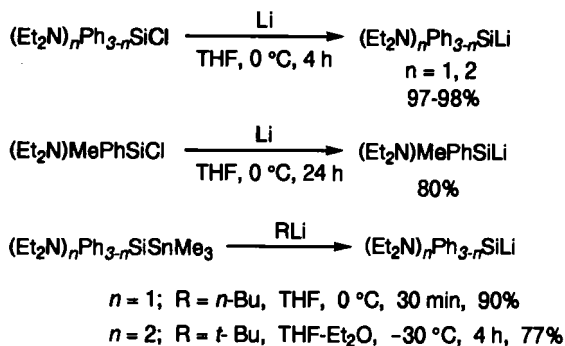
Reaction of  $\text{SiCl}_4$  with gaseous lithium (under  $10^{-4}$  torr at  $700$ – $800^\circ\text{C}$ ) appears to result in the formation of tetralithiosilane,  $\text{SiLi}_4$  (49), because quenching with excess  $\text{MeCl}$  in the presence of DME gives  $\text{Me}_4\text{Si}$  in 5–10% yields.

$\text{HPh}_2\text{SiLi}$  is prepared from  $\text{HPh}_2\text{SiCl}$  or  $\text{HPh}_2\text{SiSiPh}_2\text{H}$  with Li in THF (50). This species, however, is obtained only in low yield and readily polymerizes during prolonged reaction periods or at higher temperatures. Still, a bulky analog,  $\text{HMes}_2\text{SiLi}$  (Mes = mesityl = 2,4,6-trimethylphenyl), is obtained as stable species in good yield [Eq. (23)] (51–53). Furthermore, the off-white crystals are isolated in 71% yield (52). The  $^{29}\text{Si}$  NMR chemical shift ( $\delta -71.78$  ppm) is consistent with the presence of the electropositive lithium atom.

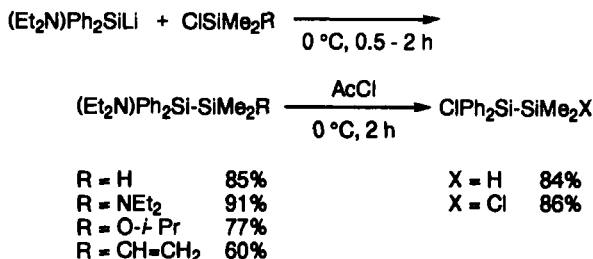


### 2. $\alpha$ -Heteroatom-Substituted Silyl Anions

Three {(amino)phenylsilyl}lithiums,  $(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$ ,  $(\text{Et}_2\text{N})_2\text{PhSiLi}$ , and  $(\text{Et}_2\text{N})\text{PhMeSiLi}$ , are obtained by (1) action of lithium metal on (amino)-phenylchlorosilanes in THF, and (2) transmetallation of the corresponding (aminosilyl)stannanes with  $\text{BuLi}$  in THF (Scheme 6) (54a–d). In method



SCHEME 6



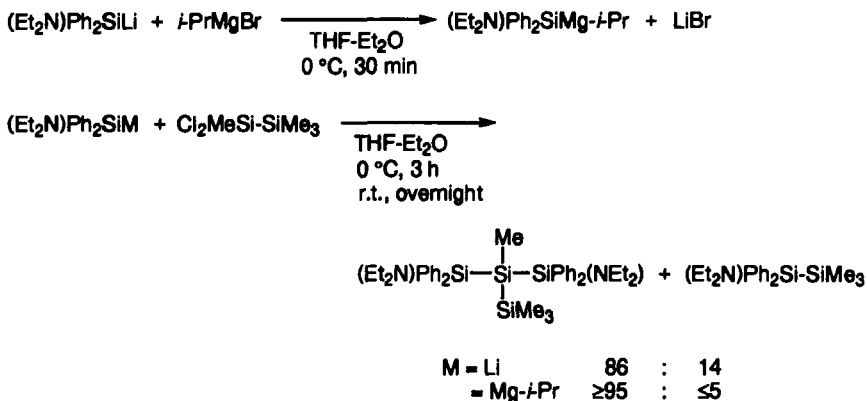
SCHEME 7

(1), a highly reactive lithium dispersion is required for preparation of the last two species.

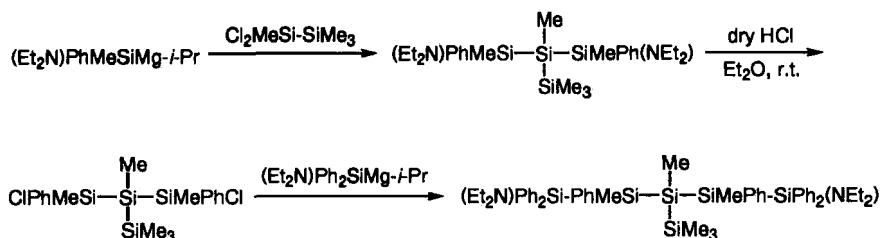
These three (aminosilyl)lithiums are stable at  $0^\circ\text{C}$  in THF for a few days under a nitrogen or argon atmosphere. The  $^{29}\text{Si}$  NMR signal of  $(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$  appears at 19.34 ppm in THF at  $0^\circ\text{C}$ . Its  $^{13}\text{C}$  chemical shifts of aromatic carbons are quite similar to those for  $\text{MePh}_2\text{SiLi}$  (19a) (data are listed in Table I in Section III-B). The result implies that the  $\text{Et}_2\text{N}$  group exhibits essentially the same effect as the Me group on the charge distribution in silyl anions (see also Section III-B).

By use of these (aminosilyl)lithiums, a variety of functional disilanes and oligosilanes are obtained. The  $\text{Et}_2\text{N}$  group on silicon can be converted into an alkoxy group or chlorine (Scheme 7). The action of lithium on (amino)alkylchlorosilanes gives not silyllithiums but instead the disilane coupling products (54c).

(Aminosilyl)magnesium species are obtained by reaction of the silyllithiums with  $i\text{-PrMgBr}$  (Scheme 8). The silylmagnesium reagents are milder



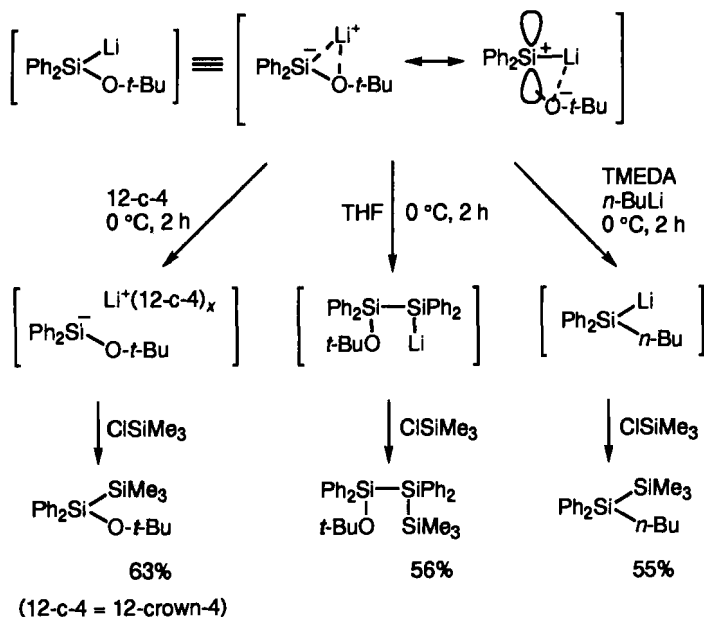
SCHEME 8



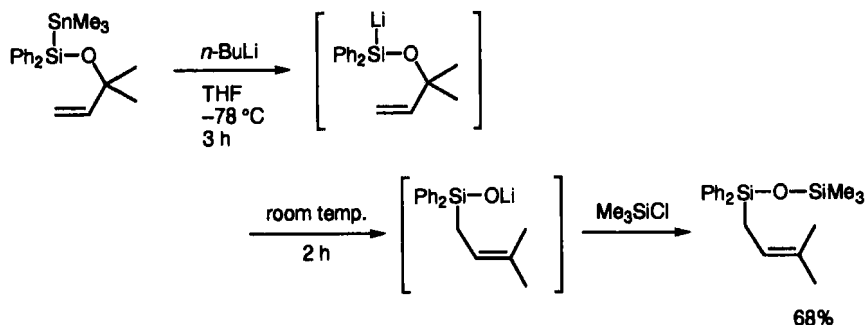
SCHEME 9

nucleophiles than the silyllithiums, so Si-Si bond cleavage is avoided in oligosilane synthesis (Schemes 8 and 9) (54b).

An (alkoxysilyl)lithium,  $(t\text{-BuO})\text{Ph}_2\text{SiLi}$ , can be prepared from  $(t\text{-BuO})\text{Ph}_2\text{SiSnMe}_3$  by treatment with  $n\text{-BuLi}$  in THF (Scheme 10). This species is stable at  $-78^\circ\text{C}$  for a few hours and behaves as an ordinary nucleophilic silyl anion (54d).  $(t\text{-BuO})\text{Ph}_2\text{SiLi}$  also behaves as an electrophile under certain conditions: It undergoes self-condensation smoothly or butylation in the presence of an excess amount of  $n\text{-BuLi}$  and TMEDA (Scheme 10).  $(t\text{-BuO})\text{Ph}_2\text{SiLi}$  thus exhibits an ambiphilic nature, that is, silylenoid character. The ambiphilic reactivity of  $(t\text{-BuO})\text{Ph}_2\text{SiLi}$ , how-



SCHEME 10



SCHEME 11

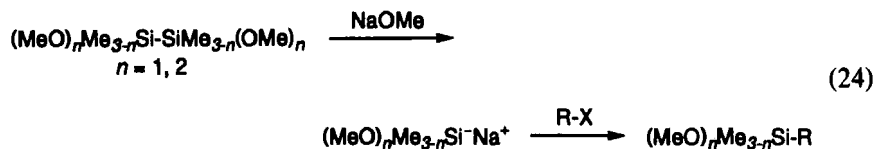
ever, disappears completely with the addition of a crown ether, which is expected to make a "solvent-separated ion pair." In this system, neither self-condensation nor butylation occurs at all (Scheme 10).

A variety of (alkoxysilyl)lithiums and other functionalized silyllithiums  $X_n\text{Ph}_{3-n}\text{SiLi}$  ( $X = t\text{-BuO}$ ,  $i\text{-PrO}$ ,  $\text{MeO}$ ,  $\text{Et}_2\text{N}$ ,  $\text{H}$ ;  $n = 1$  and  $X = t\text{-BuO}$ ;  $n = 2$ ) are obtained by reduction of the corresponding chlorosilanes with lithium 1-(dimethylamino)naphthalenide (54e).

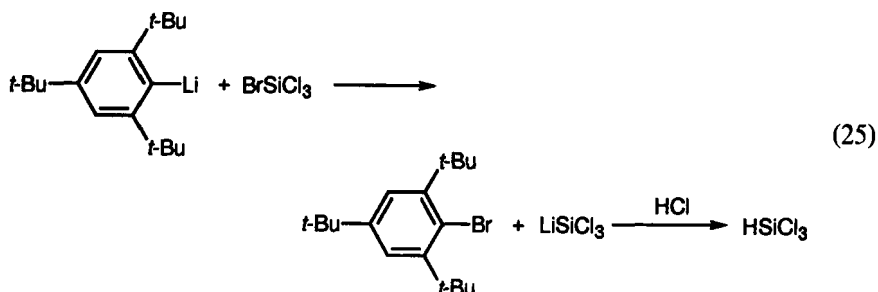
A (dialkoxysilyl)lithium  $(t\text{-BuO})_2\text{PhSiLi}$  is also obtained in 45% yield by action of lithium metal on  $(t\text{-BuO})_2\text{PhSiCl}$  in THF at  $0^\circ\text{C}$  for 4 h (54f).

(Allyloxysilyl)lithiums undergo a [2,3]Wittig-type rearrangement smoothly to form allylsilanolate anions in an intramolecular fashion (Scheme 11). This is the first example of the sila-Wittig rearrangement (54g).

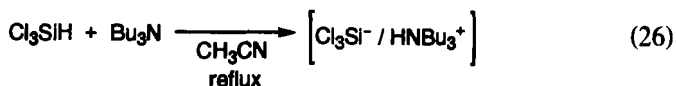
(Methoxysilyl)sodiums,  $(\text{MeO})_n\text{Me}_{3-n}\text{SiNa}$  ( $n = 1$  or  $2$ ), are generated by cleavage of the corresponding disilanes,  $(\text{MeO})_n\text{Me}_{3-n}\text{SiSiMe}_{3-n}(\text{OMe})_n$ , with  $\text{MeONa}$  in the common solvents THF, benzene, and triethylamine, requiring no strongly coordinating aprotic solvents, such as HMPA and DMI [Eq. (24)] (55a,b). This reaction is carried out in the presence of organic halides as trapping agents.



Trichlorosilyllithium,  $\text{Cl}_3\text{SiLi}$ , appears to be formed directly by a halogen-lithium exchange reaction of  $\text{Cl}_3\text{SiBr}$  with 2,4,6-tri-*t*-butylphenyllithium [Eq. (25)] (56).



Trichlorosilane,  $\text{Cl}_3\text{SiH}$ , is deprotonated by  $\text{Bu}_3\text{N}$  in refluxing  $\text{CH}_3\text{CN}$  to give a salt  $[\text{Cl}_3\text{Si}^-/\text{Bu}_3\text{NH}^+]$  [Eq. (26)] (57a-g). This species is a reductive silylating agent and is useful for organic synthesis (see Section VII). Similar species are prepared from  $\text{Cl}_3\text{SiH}$  and  $\text{Cl}_2\text{RSiH}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with TMEDA (58) (see Section VII).

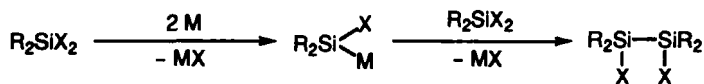


Evidence for the existence of the trichlorosilyl anion,  $\text{Cl}_3\text{Si}^-$ , has been obtained by  $^1\text{H}$  NMR. The NMR spectrum of a solution of  $\text{Cl}_3\text{SiH}$  in  $\text{CH}_3\text{CN}$  shows a sharp singlet for the  $\text{Cl}_3\text{SiH}$  proton at  $\delta$  6.25. This singlet broadens and diminishes as  $(n\text{-C}_3\text{H}_7)_3\text{N}$  is added. At the same time, a new singlet appears and grows at  $\delta$  11.03, which is attributed to the NH resonance of  $(n\text{-C}_3\text{H}_7)_3\text{NH}^+$ . This result indicates that proton exchanges are occurring between  $\text{Cl}_3\text{SiH}$  and  $(n\text{-C}_3\text{H}_7)_3\text{N}$ .

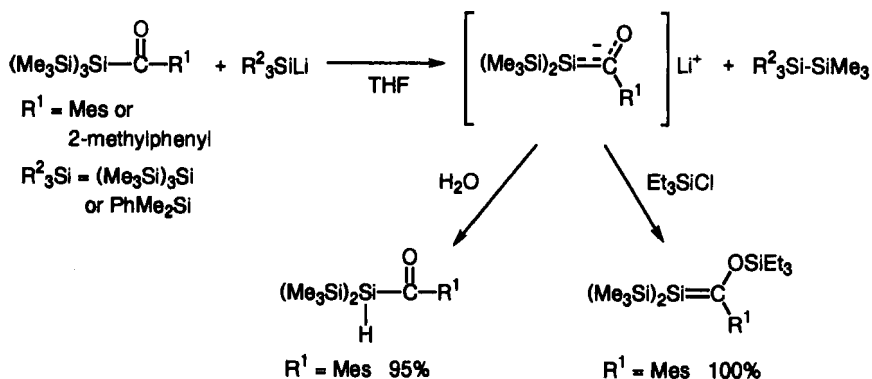
$\alpha$ -Halosilyl anions,  $\text{R}_2\text{Si}(\text{X})(\text{M})$ , are postulated intermediates in polysilane synthesis via reductive coupling of dihalosilanes with alkali metal. The  $\alpha$ -halosilyl anion generated from dihalosilane and alkali metal rapidly undergoes coupling with dihalosilane to give dihalodisilane (Scheme 12) (59) (see also Section VI-B). A theoretical study on (fluorosilyl)lithium,  $\text{H}_2\text{SiLiF}$ , has been performed (see Section VIII).

### 3. Sila-Enolate

Silyl anions in which a carbonyl group is attached to silicon have been reported (60). An acyltris(trimethylsilyl)silane is treated with tris(trimeth-



SCHEME 12



SCHEME 13

ylsilyl)silyllithium in THF at  $-80^\circ\text{C}$  for 2 hours to give a silicon analog of a lithium enolate, along with quantitative amount of tetrakis(trimethylsilyl)silane (Scheme 13). The lithium sila-enolate is trapped by  $\text{H}_2\text{O}$  to give the corresponding acylbis(trimethylsilyl)silane in 95% yield. In contrast, trapping by  $\text{Et}_3\text{SiCl}$  gives the corresponding sila-enol silyl ether (siloxy-silene) in quantitative yield. The  $^1\text{H}$  NMR spectrum of the enolate in THF at  $-40^\circ\text{C}$  shows two resonances, at  $-0.26$  and  $0.17$  ppm, attributed to two nonequivalent trimethylsilyl protons. The  $^{29}\text{Si}$  NMR spectrum at  $-40^\circ\text{C}$  shows three resonances, at  $-10.6$ ,  $-12.8$ , and  $-59.9$  ppm, attributed to two nonequivalent trimethylsilyl silicons and central silicon, respectively.

The formation of the sila-enolate has been supported by theoretical calculations (6-31G\*) for a model reaction as shown in Eq. (27). The enthalpy for this reaction has been calculated to be  $-13.81$  kcal/mol. The formation of the sila-enolate is thus thermodynamically favorable.



#### 4. Silacyclopentadienide Anions

Studies on silacyclopentadienide anions have been developing in recent years (61). The term *silole* means the same thing as *silacyclopentadiene*.

Theoretical calculations on a model system have predicted that the ground-state conformation of the anion is the pyramidal  $C_s$  structure (Fig. 5) (62). It is noteworthy that the  $C_s$  structure has unusually long C-Si bonds and a butadiene-like geometry of the carbon skeleton. The planar  $C_{2v}$  form is the transition state for pyramidal inversion between equivalent  $C_s$  structures, the inversion barrier being  $16.2$  kcal/mol (6-31 G\*).

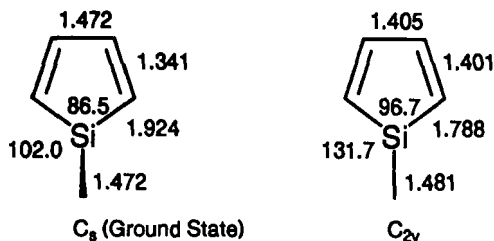
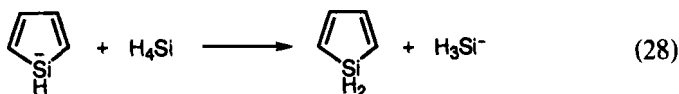
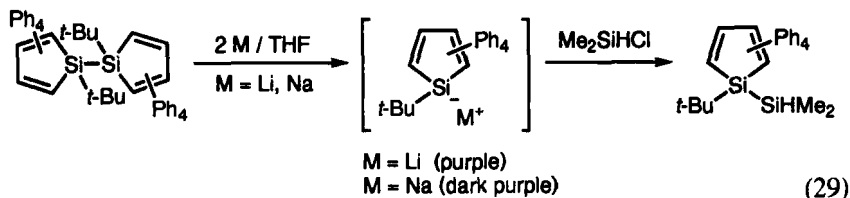


FIG. 5. Calculated bonding parameters for two conformations of a cyclopentadienide anion. Bond lengths are in angstroms and bond angles in degrees.

An energy difference for the isodesmic reaction [Eq. (28)] indicates a quantitative measure of the extent of electron delocalization (6-31G\*) (62). The energy difference for the  $C_s$  structure of the silacyclopentadienide anion is only 2.2 kcal/mol, which is much smaller than 73.4 kcal/mol for the carbon analog, a planar cyclopentadienide anion ( $C_{2v}$ ). On the basis of these calculations, it is concluded that the ground-state structure of the silacyclopentadienide anion has only ca. 3% of the resonance stabilization exhibited by the cyclopentadienide anion. However, the previous calculation (3-21G//STO-2G) on the  $C_{2v}$  planar structure shows that the resonance energy is 23 kcal/mol, which means ca. 25% as aromatic as the carbon analog (63).

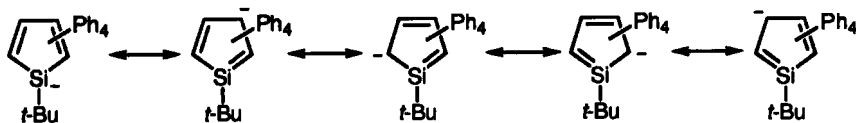


1-Lithio- and 1-sodio-1-*t*-butyl-2,3,4,5-tetraphenylsilacyclopentadienes are prepared by cleavage of the Si-Si bond of di(silacyclopentadienyl) with Li and Na, respectively, in THF at room temperature [Eq. (29)] (64a).



The  $^{29}\text{Si}$  NMR chemical shifts are observed at 25.10 ppm for the lithio derivative and at 26.12 ppm for the sodio derivative, a large downfield shift compared to the starting material (3.62 ppm). The downfield shifts strongly suggest the incorporation of silicon *p*-orbitals to diffuse and/or



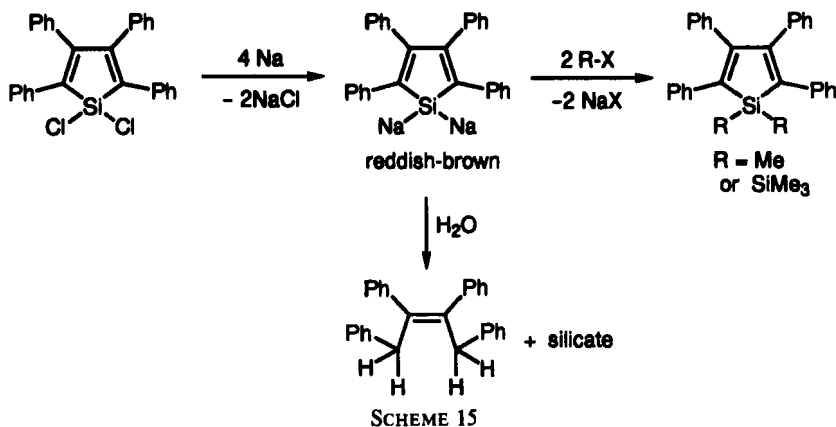


SCHEME 14

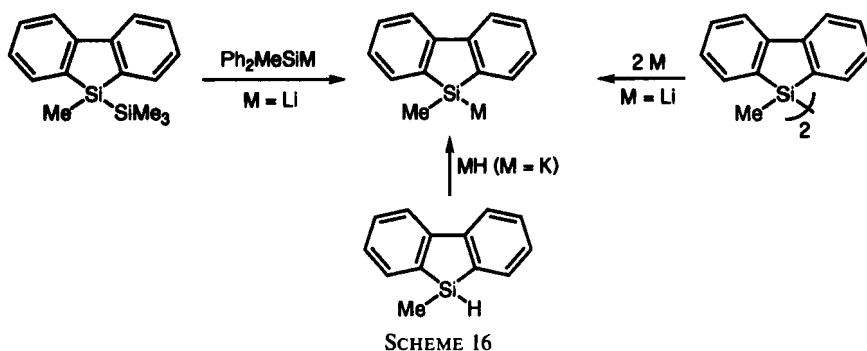
delocalize the negative charge into the butadiene moiety (Scheme 14). In the  $^{13}\text{C}$  NMR spectrum of the lithio derivative, the  $\text{C}_\alpha$  and  $\text{C}_\beta$  are shifted upfield ( $\Delta\delta = -5.26$  and  $-2.28$  ppm), the ipso and ortho carbons,  $\text{C}_i$  and  $\text{C}_o$ , of the four phenyl groups are shifted downfield ( $\Delta\delta = 1.10$  and  $7.03$  ppm), and the meta and para carbons,  $\text{C}_m$  and  $\text{C}_p$ , are shifted upfield ( $\Delta\delta = -1.19$  and  $-4.92$  ppm). The upfield shielding of the  $\text{C}_\alpha$  and  $\text{C}_\beta$  in the anion indicates that there is an increase in  $\pi$ -electron density at these positions, as shown in Scheme 14. The four phenyl groups on the ring provide additional stabilization of the silacyclopentadienyl anion through polarization (*cf.* Fig. 2).

1-Lithio-1-methyl-2,3,4,5-tetraphenylsilacyclopentadiene is also prepared and characterized by X-ray analysis which shows a dimeric structure containing a 1,3-disilacyclobutane skeleton formed in such a fashion that each silyl anion adds to the C2-C3 double bond in the other ring (64b).

1,1-Disodio-2,3,4,5-tetraphenyl-1-silacyclopentadiene is obtained as a reddish-brown solid from the 1,1-dichloro derivative, with more than four equivalents of Na in refluxing dioxane for 7 hours in 80% yield (Scheme 15) (65a). Reaction of the dianion with MeI and  $\text{Me}_3\text{SiCl}$  gives the expected trapping products. Trapping with  $\text{H}_2\text{O}$ , however, causes ring opening to give 1,2,3,4-tetraphenyl-2-butene and silicate.



SCHEME 15



1,1-Dilithio-silacyclopentadienes are also prepared from the 1,1-dichloroderivatives with four equivalents of lithium in THF (65*b,c,d*). X-ray analysis indicates a monomeric structure in which one lithium atom lies in the plane and the other over the plane of the silacyclopentadiene ring, thus represented as  $\eta^5$ -(1-lithio-silacyclopentadienyl)lithium (65*d*).

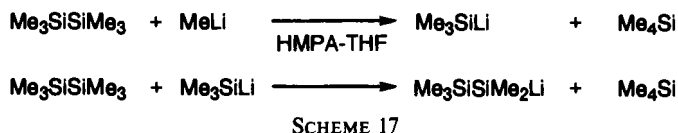
Benzosilole anions have been obtained in three ways, as summarized in Scheme 16. 5-Lithio-5-methyldibenzosilole is thus obtained from bis(dibenzosilole) with lithium in THF, which affords 5,5-dimethyldibenzosilole (54% yield) after trapping by dimethyl sulfate (66). The same species is also formed from 5-methyl-5-(trimethylsilyl)dibenzosilole via the Si-Si bond cleavage on treatment with  $\text{Ph}_2\text{MeSiLi}$  in THF at  $-78^\circ\text{C}$ , together with tetramethyldiphenyldisilane (67). The potassium analog can be prepared from the 1-hydridobenzosilole by treatment with strong nonnucleophilic bases such as KH (14).

The  $^1\text{H}$  NMR spectrum of the lithium species reveals a sharp resonance at  $\delta$  0.24 ppm due to the  $\text{CH}_3$ -Si protons. The UV spectrum of the anion in THF exhibits characteristic absorptions in the longer-wavelength region at 377 nm ( $\epsilon$  5700) and 546 nm ( $\epsilon$  1200), in comparison with the neutral dibenzosilole, which has several absorption maxima up to 318 nm ( $\epsilon$  170).

## VI

### POLYSILANYL ANIONS

These species may fall into two classes: isolable or spectroscopically detectable polysilanyl anions, and polysilanyl anions postulated as reaction intermediates.



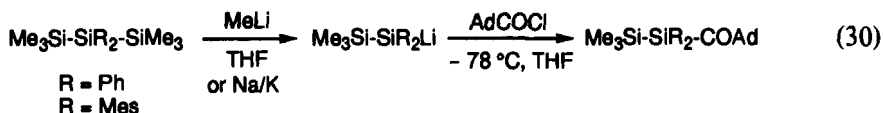
## A. Preparation, Reaction, and Structure

### 1. Disilanyl Anions

Polysilanyl anions,  $\text{H}_3\text{SiH}_2\text{SiK}$ ,  $(\text{H}_3\text{Si})_2\text{HSiK}$ , and  $(\text{H}_3\text{Si})_3\text{SiK}$ , are prepared, respectively, (a) from  $\text{H}_3\text{SiK}$  with  $\text{SiH}_4$ , (b) from  $\text{H}_3\text{SiK}$  and  $\text{Si}_3\text{H}_8$ , and (c) from  $\text{Si}_2\text{H}_6$  or  $\text{Si}_3\text{H}_8$  and K in HMPA, and identified by  $^1\text{H}$  NMR and IR spectroscopy (46) (see also Section V).

As mentioned in Section IV-A,  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  is prepared by the action of MeLi on  $\text{Me}_3\text{SiSiMe}_3$  on a large scale (Scheme 17) (68a–c). It is proposed that in this reaction,  $\text{Me}_3\text{SiLi}$ , resulting from Si–Si bond cleavage by MeLi in the first stage, cleaves the Si–C(methyl) bond of the unreacted disilane to give  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  and  $\text{Me}_4\text{Si}$  (68a). This reaction occurs also with *n*-BuLi instead of MeLi. A similar Si–C(methyl) bond cleavage is also observed in the case of dodecamethylcyclohexasilane (see Section VII-A-4).

The Si–Si bond cleavage of trisilanes by MeLi in THF is applicable to the preparation of disilanylolithiums, in which a phenyl or mesityl group is attached to  $\alpha$ -silicon [Eq. (30)] (69). A similar cleavage reaction occurs with a Na/K alloy to afford disilanylpotassium. These species couple with  $\text{AdCOCl}$  (Ad = 1-adamantyl) to give acyldisilane in modest yields.



A mercury–lithium exchange reaction of  $(\text{Me}_3\text{SiMe}_2\text{Si})_2\text{Hg}$  yields  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  in toluene quantitatively (Scheme 18) (70). Similarly, a variety of polysilanylolithiums is also obtained (see Section VI-A-3). This method can avoid polar solvents, so the reagents undergo coupling reactions with chlorosilanes, without undesirable Si–Si bond cleavage, to afford various oligosilanes in high yields (see Section VI-A-3).

The  $^{29}\text{Si}$  NMR signals of  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  are observed at  $-74.9$  ppm for  $\alpha$ -silicon (bonded to Li) and at  $-12.4$  ppm for  $\beta$ -silicon (in trimethylsilyl) in  $\text{THF-d}_8$  solution. These data indicate that the negative charge is highly localized on the  $\alpha$ -silicon atom. At 180 K, the  $\alpha$ -silicon is observed as a

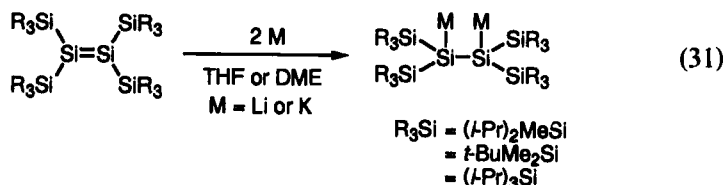
**SCHEME 18**

A disilanylene 1,2-dianion is formed in the reaction of 1,2-dichloro-1,2-disilaacenaphthene with lithium in THF under ultrasonication (Scheme 19) (71). Trapping with MeI and CH<sub>3</sub>OD gives the corresponding dimethyl- and dideuterio-disilaacenaphthene, respectively. It is emphasized that the action of lithium on the dichlorodisilane gives not disilene but disilanylene dianion. This may result because the distance between two silicon atoms of the starting material is fixed at Si–Si single bond length by the naphthalene skeleton, inhibiting Si–Si double bond formation.

**SCHEME 19**

The resulting dianion decomposes at room temperature with a half-life of 13.5 hours at 30°C. The  $^{29}\text{Si}$  resonance is observed at  $-1.24$  ppm, shifted upfield relative to that of the starting dichlorodisilane (8.99 ppm). The  $^{13}\text{C}$  NMR spectrum shows that the ipso carbon on the naphthalene ring (172.94 ppm) shifts remarkably downfield relative to the starting material (136.23 ppm). This may be caused by the  $\pi$ -polarization effect of the naphthyl ring as observed in the case of (phenylsilyl)lithiums (see section III-B).

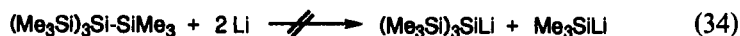
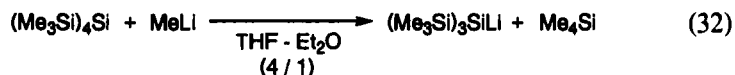
Reduction of tetrakis(trialkylsilyl) disilene with Li in THF or K in DME gives the corresponding 1,2-dianions, together with the anion radicals [Eq. (31)] (72).



## 2. Tris(trimethylsilyl)silyllithium, $(\text{Me}_3\text{Si})_3\text{SiLi}$ , and Its Analogues

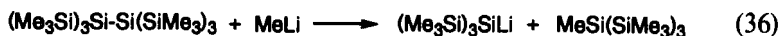
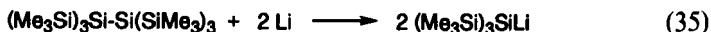
Tris(trimethylsilyl)silyllithium,  $(\text{Me}_3\text{Si})_3\text{SiLi}$ , and its derivatives that contain branched silicon chains are the most extensively investigated species among polysilanyllithiums.

Tetrakis(trimethylsilyl)silane,  $(\text{Me}_3\text{Si})_4\text{Si}$ , undergoes cleavage of the Si-Si bond with MeLi in THF/Et<sub>2</sub>O (4/1) to give a pale greenish-yellow solution of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  [Eq. (32)] (73a). Tris(dimethylsilyl)silyllithium,  $(\text{HMe}_2\text{Si})_3\text{SiLi}$ , is obtained from  $(\text{HMe}_2\text{Si})_4\text{Si}$  by a similar method (73a).  $\text{Ph}_3\text{SiLi}$  is applicable to the cleavage, indicative of the higher stability of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  than  $\text{Ph}_3\text{SiLi}$ ; the reverse reaction results in the recovery of the starting materials [Eq. (33)] (73b).  $(\text{Me}_3\text{Si})_3\text{SiLi}$  cannot be prepared by the reaction of  $(\text{Me}_3\text{Si})_4\text{Si}$  and lithium metal; this may be ascribed to the formation of the thermodynamically less stable  $\text{Me}_3\text{SiLi}$  [Eq. (34)] (73b).



In contrast, hexakis(trimethylsilyl)disilane,  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_3$ , is cleaved with lithium metal in THF [Eq. (35)] (73c), as well as with MeLi

[Eq. (36)] (74) regioselectively, to give  $(\text{Me}_3\text{Si})_3\text{SiLi}$ . Exposure of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  to the disilane yields  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{Me}_3\text{Si})_2\text{Li}$  and  $\text{Li}(\text{Me}_3\text{Si})_2\text{SiSi}(\text{Me}_3\text{Si})_2\text{Li}$  [Eq. (37)] (73c).



These results imply that the stability increases in the following order:  $\text{Me}_3\text{SiLi}$ ,  $\text{Ph}_3\text{SiLi} < \text{Me}_3\text{SiMe}_2\text{SiLi} < (\text{Me}_3\text{Si})_3\text{SiLi} < (\text{Me}_3\text{Si})_3\text{SiSi}(\text{Me}_3\text{Si})_2\text{Li}$ . In terms of inductive effect, one would expect  $\text{Me}_3\text{SiLi}$  to be more stable than  $(\text{Me}_3\text{Si})_3\text{SiLi}$ , since a trimethylsilyl group is a better electron donor than is a methyl group. The facts, however, are opposite. In the original paper, the stability of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  was explained by the conjugation effect between the vacant  $3d$  orbitals of peripheral silicon atoms (the electron acceptors) and the filled  $3p$  orbital of the lithium-bearing silicon atom (the electron donor) (dative  $p\pi-d\pi$  bonding) (73b). However, the stabilization now may be explained by hyperconjugative mixing of the anion  $3p$  ( $\text{Si}_\alpha$ ) with  $\sigma^*$  ( $\text{Si}_\beta\text{-C}$ ) orbitals.

$(\text{Me}_3\text{Si})_3\text{SiLi}$  decomposes slowly in THF. This problem is avoided by a solvent-exchange technique. The silyllithium is isolated as a colorless crystalline solid containing three mole-equivalents of THF of solvation, that is,  $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$  (75). The compound is soluble in hydrocarbon solvents, giving a colorless solution, and coupling reactions in such nonpolar media are generally much cleaner and higher in yield.

The UV spectra in THF show absorption maxima at 236 nm ( $\epsilon$  6000, sh), 295 nm ( $\epsilon$  22000), and 370 nm ( $\epsilon$  10000), whereas its neutral derivatives,  $(\text{Me}_3\text{Si})_4\text{Si}$  and  $(\text{Me}_3\text{Si})_3\text{SiH}$ , show no absorption above 210 nm (cyclohexane) (73b). These marked absorptions of long wavelengths imply considerable resonance stabilization, as mentioned earlier. The  $^{29}\text{Si}$  NMR signal ( $\text{C}_6\text{D}_6$ ) is observed at much higher field ( $-185.4$  ppm) for the central silicon in the anion than that for the central silicon of  $(\text{Me}_3\text{Si})_4\text{Si}$  ( $-135.5$  ppm) (75). The  $^{29}\text{Si}$  resonance is observed at  $-189.4$  ppm in  $\text{C}_7\text{H}_8\text{-C}_6\text{D}_6$  at room temperature and resolves into a quartet due to coupling with one  $^7\text{Li}$  atom ( $I = 3/2$ ,  $^1J[^{29}\text{Si}, ^7\text{Li}] = 38.6$  Hz). This result implies a partial covalent nature of the Si-Li bond (76a).

The crystal structure of  $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$  has been determined by X-ray analysis (Fig. 6) (22,76). There is distorted tetrahedral coordination at both lithium and silicon. The Si-Li bond length is  $2.67 \text{ \AA}$ , which is similar to the average Li-Si bond length ( $2.68 \text{ \AA}$ ) observed in  $(\text{Me}_3\text{SiLi})_6$

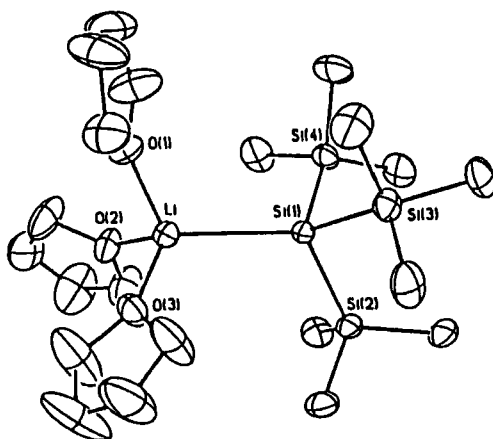
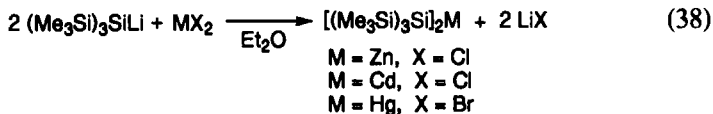


FIG. 6. Computer-generated thermal ellipsoidal drawing of  $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 3\text{THF}$  (22). Reprinted with permission from *J. Organomet. Chem.* **1993**, 462, 1. Copyright (1993) Elsevier Science S. A.

(see section IV-B). In addition, it is slightly longer than the Li–Si bonds ( $2.63 \text{ \AA}$ ) observed in  $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 1.5\text{DME}$  (77). The average Si–Si distance is  $2.33 \text{ \AA}$ . For the central silicon atom, the average Si–Si–Si and Si–Si–Li bond angles are  $103^\circ$  and  $116^\circ$ , respectively. The geometry of the  $(\text{Me}_3\text{Si})_3\text{Si}$ -moiety thus indicates increased *s*-character in the silicon orbital directed toward lithium.

$(\text{Me}_3\text{Si})_3\text{SiM}$  ( $\text{M} = \text{K}, \text{Rb}, \text{and Cs}$ ) can be obtained by the metal–metal exchange reaction of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{M}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$ ) with the corresponding alkali metals in *n*-pentane (78). These compounds are colorless powders in their pure solvent-free state. The X-ray structure analyses reveal their dimeric molecular structures.

Reaction of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  with  $\text{MX}_2$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}; \text{X} = \text{halide}$ ) in  $\text{Et}_2\text{O}$  yields  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{M}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ) [Eq. (38)] (79a). The Si–Tl and Si–Pb compounds cannot be obtained from  $(\text{Me}_3\text{Si})_3\text{SiLi}$  with the metal halides, the reaction affording the elemental metals and  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_3$  (76, 79b, 80a).



While the zinc and mercury derivatives are stable in benzene- $d_6$  solution for at least 3 days, the cadmium derivative is much less stable. The  $^{29}\text{Si}$  NMR shifts for these compounds move to lower field on descending the

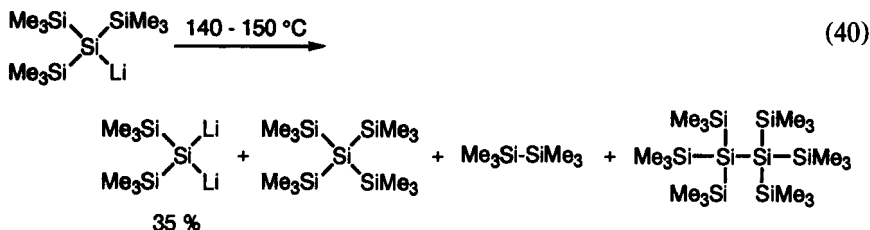
group from zinc to mercury (79a). X-ray crystal structure analysis of the zinc derivative reveals that the compound adopts a  $D_{3d}$  structure in the solid state, with the central zinc atom lying at the inversion center (79a). The two  $(\text{Me}_3\text{Si})_3\text{Si}$ -ligands are bonded in a linear fashion to the metal ( $\text{Si}-\text{Zn}-\text{Si}$  angle =  $180^\circ$ ). The  $\text{Zn}-\text{Si}$  bond distance, 2.34 Å, is close to that expected on the basis of covalent radii [2.35 Å, from covalent radii for Zn (1.18 Å) and for Si (1.17 Å)]. The average  $\text{Si}-\text{Si}-\text{Si}$  angle is  $112^\circ$ , which is larger than that of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  ( $103^\circ$ ). The average  $\text{Si}-\text{Si}-\text{Zn}$  angle is  $107^\circ$ .

Silylcuprates  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Cu}_2\text{Cl}_4(\text{Li}\cdot 4\text{THF})$  and  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Cu}_2\text{Br}(\text{Li}\cdot 3\text{THF})$  are prepared by reaction of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  with, respectively,  $\text{CuCl}$  in pentane-THF and  $\text{CuBr}$  in hexane-THF (76,80). X-ray analysis of these silylcuprates shows the presence of a bridging  $(\text{Me}_3\text{Si})_3\text{Si}$  group on a  $\text{Cu}-\text{Cu}$  bond in both cases (80b,c).

A tin-substituted silyllithium  $(\text{Me}_3\text{Sn})_3\text{SiLi}$  is prepared by reaction of  $(\text{Me}_3\text{Sn})_4\text{Si}$  with  $\text{MeLi}$  [Eq. (39)] (81a,b). The compound is obtained in 81% yield as light yellow crystals from pentane. The  $^{29}\text{Si}$  NMR shift for  $(\text{Me}_3\text{Sn})_3\text{SiLi}$ ,  $-122.0$  ppm, is upfield from that of  $(\text{Me}_3\text{Sn})_4\text{Si}$ ,  $-69.2$  ppm, and is downfield from the analogous  $(\text{Me}_3\text{Si})_3\text{SiLi}$  ( $-184.5$  ppm).



A *gem*-dilithiooligosilane,  $(\text{Me}_3\text{Si})_2\text{SiLi}_2$ , is prepared by thermal redistribution of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  at  $140-150^\circ\text{C}$  [Eq. (40)] (82). If the reaction is carried out for a longer time, the coupling product  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_3$  is produced at the expense of the dilithio compound. Flash-vaporization mass spectroscopy of a solid sample of  $(\text{Me}_3\text{Si})_2\text{SiLi}_2$  displays parent ions for both the monomer and the dimer.

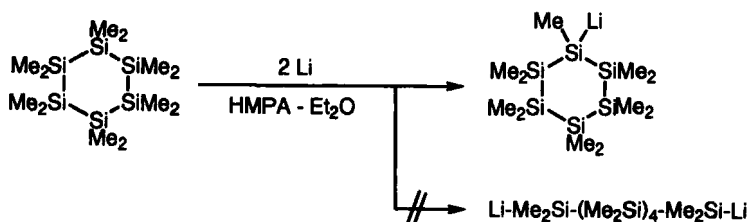


### 3. Linear Oligosilanyllithiums

Action of lithium metal on linear phenyloligosilanes gives rise to the  $\text{Si}-\text{Si}$  bond cleavage with no regioselectivity to yield a mixture of various mono- and oligosilanyllithiums (83). In contrast, action of lithium metal







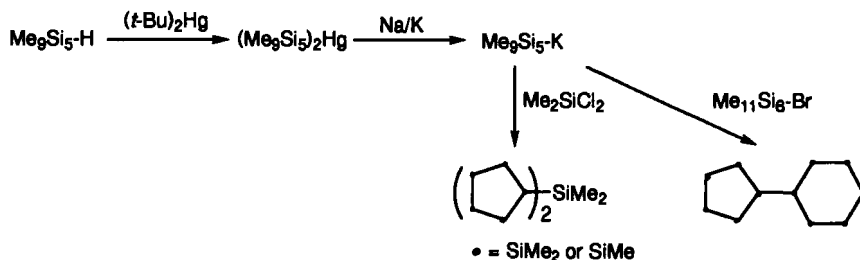
SCHEME 21

the presence of excess amounts of Li (4 equivalents),  $\text{Me}_{11}\text{Si}_6\text{Li}$  is inert to further Si-C bond cleavage. A sealed solution of  $\text{Me}_{11}\text{Si}_6\text{Li}$  in HMPA is stable for weeks at room temperature in the dark. The anion can be trapped with various agents, such as bromoethane and trimethylchlorosilane, to give the expected products in nearly 50% yield.

Treatment of the cyclohexasilane with MeLi, PhLi, or metal alkoxides ROM ( $\text{M} = \text{Na}, \text{K}$ ;  $\text{R} = \text{Me}, \text{Et}, t\text{-Bu}$ ) in HMPA/ $\text{Et}_2\text{O}$  offers additional routes to the anion (86). Some linear oligosilanes are also formed, due to concomitant ring cleavage. Reaction of decamethylcyclopentasilane,  $(\text{Me}_2\text{Si})_5$ , with MeLi in HMPA does not give cyclopentasilanyllithium but rather species resulting from ring cleavage.

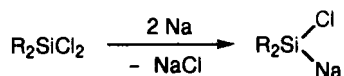
The thermodynamic stability of  $\text{Me}_{11}\text{Si}_6\text{Li}$  may be due to the electron delocalization onto the contiguous silicon framework, consistent with the increasing order of thermodynamic stability:  $\text{Me}_3\text{SiLi} < (\text{Me}_3\text{Si})\text{Me}_2\text{SiLi} < (\text{Me}_3\text{Si})_3\text{SiLi}$  (73b). The  $^{29}\text{Si}$  NMR spectrum of  $\text{Me}_{11}\text{Si}_6\text{Li}$  shows four sharp singlets, at  $\delta -108.1, -33.8, -40.7$ , and  $-41.6$  ppm, with a 1 : 2 : 2 : 1 ratio: The highest field peak can be assigned to the negatively charged silicon.

Nonamethylcyclopentasilanyl-potassium,  $\text{Me}_9\text{Si}_5\text{K}$ , can be prepared via a mercury-potassium exchange reaction from bis(cyclopentasilanyl)mercury,  $(\text{Me}_9\text{Si}_5)_2\text{Hg}$ , which is obtained by the reaction of hydro-cyclopentasilane with  $(t\text{-Bu})_2\text{Hg}$  (Scheme 22) (87). This potassium reagent offers a new route to permethylated polycyclic polysilanes.

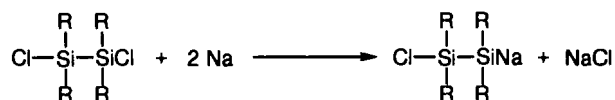
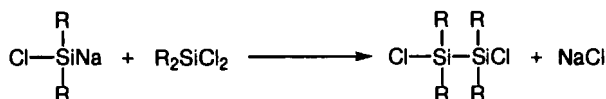


SCHEME 22

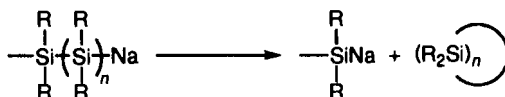
## Initiation



## Propagation



## Back-biting



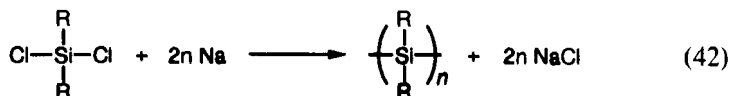
SCHEME 23

## B. Intermediates in Polysilane Syntheses

Polysilanyl anions are reactive intermediates in various synthetic routes to polysilanes.

## 1. Reductive Coupling of Dichlorosilanes and Related Reactions

In the Wurtz coupling reaction of dichlorosilanes with sodium to polysilanes [Eq. (42)], polysilanyl anions are considered to be crucial reaction intermediates in the propagation step and in the cyclization via back-biting (Scheme 23) (88).



The reduction of  $\text{Me}_2\text{SiCl}_2$  with sodium-potassium alloy in THF forms dodecamethylcyclohexasilane,  $(\text{Me}_2\text{Si})_6$ , as the major product, in two stages. In the first stage, the main product is  $(\text{Me}_2\text{Si})_n$  polymer. After all

$$\text{Me}_2\text{SiCl}_2 \xrightarrow[\text{THF}]{\text{Li, Ph}_3\text{SiSiMe}_3} (\text{Me}_2\text{Si})_6 + (\text{Me}_2\text{Si})_5 + (\text{Me}_2\text{Si})_7 \quad (43)$$

90%                      9%                      1%

$$\text{PhMe}_2\text{Si}(\text{Me}_2\text{Si})_n\text{SiMe}_2\text{Ph} \xrightarrow[\text{THF}]{\text{PhMe}_2\text{SiLi}} (\text{Me}_2\text{Si})_8 + \text{PhMe}_2\text{Si}(\text{Me}_2\text{Si})_x\text{SiMe}_2\text{Ph} \quad (44)$$

$n = 1-3$                        $x = 0-3$

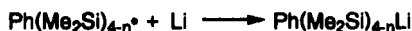
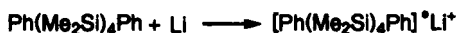
$$\text{Ph}(\text{Me}_2\text{Si})_2\text{Cl} + 2 \text{Li} \xrightarrow{-\text{LiCl}} \text{Ph}(\text{Me}_2\text{Si})_x\text{Li} \rightleftharpoons 1/6 (\text{Me}_2\text{Si})_6 + \text{PhMe}_2\text{SiLi}$$

**SCHEME 24**

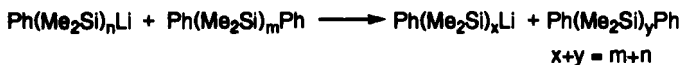
## stage 1



## stage 2



## stage 3



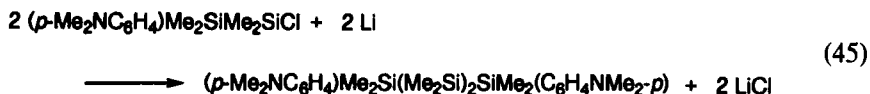
## stage 4



SCHEME 25

at this stage. Stage 3 starts when the disilanyl chloride is completely consumed. As the concentration of the linear oligosilanes decreases, the cyclohexasilane appears. The consumption of lithium continues throughout stage 3. The silyl anions, which have a longer lifetime in this stage, cleave the Si-Si bonds, resulting in the scrambling processes. The intermediate silyl anions are generated continuously and provide routes to cyclic oligosilanes. The relative concentrations of cyclic to linear oligosilanes are determined by their relative stabilities, i.e., by thermodynamics. In stage 4, the oligosilanes are cleaved by the continuous donation of electrons from lithium to lead to the formation of radical anions and anions. A thermodynamic mixture of monosilyl anions, disilanyl anions, and the cyclohexasilane is produced.

Electron-donating substituents on the aromatic rings decrease the electron affinity of the oligosilanes. 1-Chloro-2-*p*-(dimethylamino)phenyl]tetramethyldisilane thus reacts with lithium to form exclusively the tetrasilane that is stable in the presence of excess Li metal [Eq. (45)].

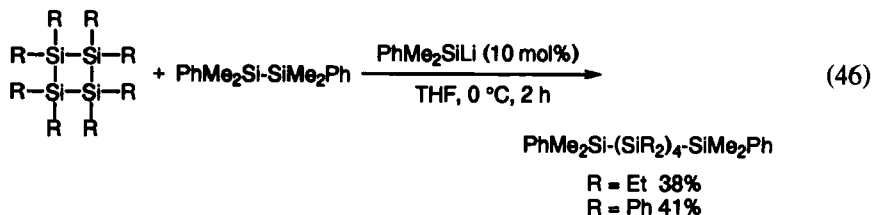


## 2. Oligomerization

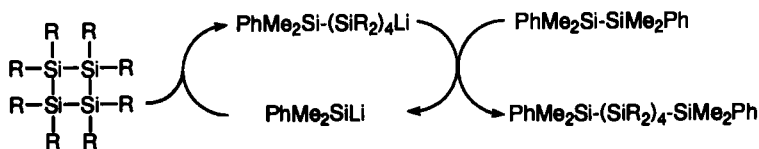
The action of a catalytic amount of MeONa on methoxymethyldisilane gives  $\alpha,\omega$ -dimethoxypermethylpolysilanes or cyclic polysilanes, depending on the reaction time (55*b*). It was concluded that the mechanism involves a concerted nucleophilic substitution with base-assistance or stepwise substitution by silyl anion; a silylene mechanism is ruled out.

## 3. Ring-Opening Polymerization of Cyclotetrasilanes and Cyclopentasilanes

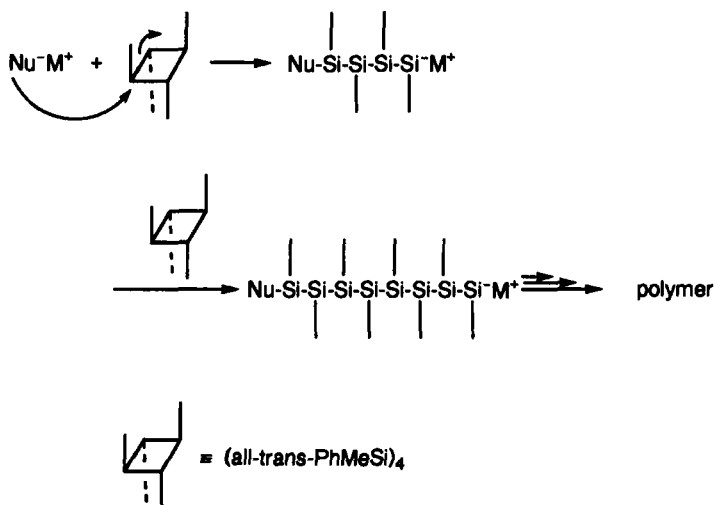
Cyclotetrasilanes undergo ring-opening by the action of a variety of nucleophiles, such as silyl anions and fluoride anion, to form the corresponding oligosilanyl anions. In the presence of 1,2-diphenyltetramethyldisilane, the oligosilanyl anions are trapped efficiently, resulting in the ring-opening disilylation of cyclotetrasilanes [Eq. (46)] (92): The reaction proceeds catalytically with respect to  $\text{PhMe}_2\text{SiLi}$  (Scheme 26).



Reaction of tetramethyltetraphenylcyclotetrasilanes  $(\text{PhMeSi})_4$  with a catalytic amount of butyllithium, silylpotassium or silylcuprate,  $(\text{PhMe}_2\text{Si})_2\text{CuLi}$ , brings about anionic ring-opening polymerization (Scheme 27) (93); the ring strain of the tetrasilane is sufficient for subsequent ring-opening to cause completion of polymerization before the depolymerization due to back-biting becomes significant. Phenylnonamethylcyclopenten-

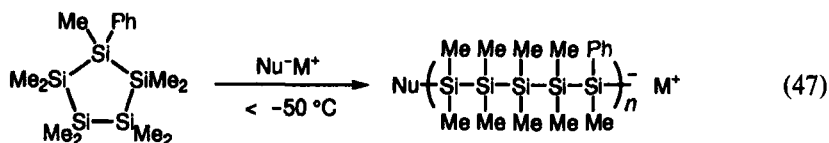


SCHEME 26



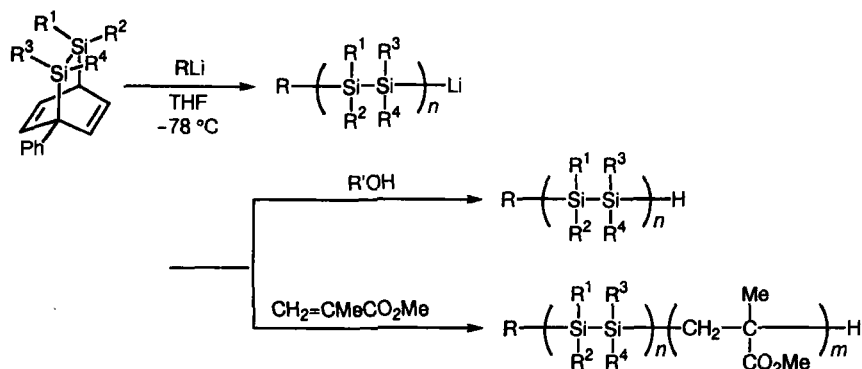
SCHEME 27

tasilane undergoes anionic ring-opening polymerization induced by a catalytic amount of  $\text{Bu}_4\text{NF}$ ,  $\text{Me}_3\text{SiK}$ , or  $\text{PhMe}_2\text{SiK}$  in polar solvents at low temperatures ( $< -50^\circ\text{C}$ ) [Eq. (47)] (94). The ring-opening is regioselective in such a way that the phenyl-bearing silyl anion is formed in every step. At higher temperatures, only a mixture of cyclic oligomers results.



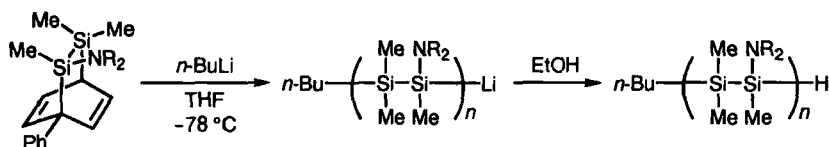
#### 4. Anionic Polymerization of Masked Disilenes

Anionic polymerization of masked disilenes has opened up a novel route to polysilanes (95). 1-Phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes can be used as masked disilenes.  $n\text{-BuLi}$  works as an initiator. The polymerization may involve the attack of the polysilanyl anions on a silicon atom of the monomer, resulting in the formation of the new propagating polymer anion and biphenyl. This method is applicable to aminopolysilane synthesis (Scheme 28).



$\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4 = \text{Me}, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, \text{ or } n\text{-C}_6\text{H}_{13}$

$\text{R} = \text{Me}, n\text{-Bu}, \text{sec-Bu}, \text{Ph}$



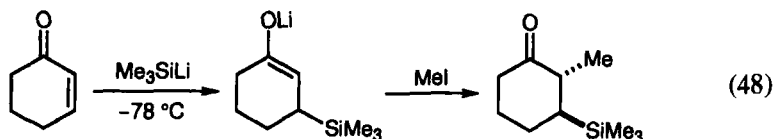
SCHEME 28

## VII

### SYNTHETIC APPLICATION OF SILYL ANIONS

Certain silyl anions are useful silylating reagents in organic synthesis. Since some leading reviews have covered the synthetic applications (*Id,ef,2*), only a few typical examples are mentioned here.

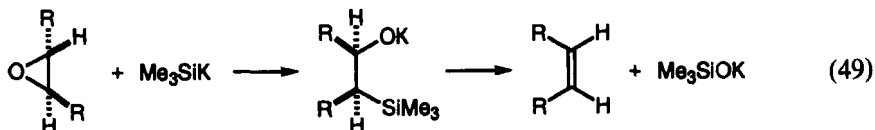
$\text{Me}_3\text{SiLi}$  undergoes smoothly conjugate addition to  $\alpha,\beta$ -unsaturated ketones in the absence of copper salt [Eq. (48)] (29).



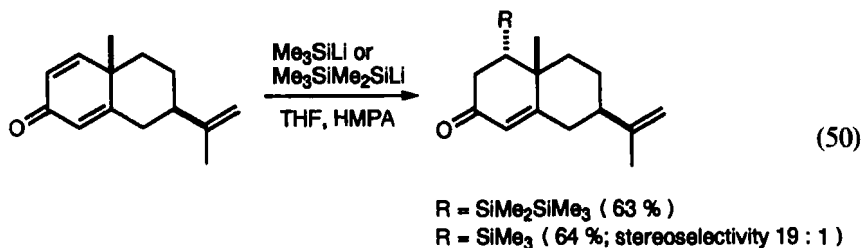
By use of  $\text{Me}_3\text{SiK}$ , some mono-, di-, and trisubstituted epoxides can be deoxygenated stereospecifically, with inversion of stereochemistry [Eq. (49)] (96, 97). Thus, reaction of *cis* and *trans* epoxides with  $\text{Me}_3\text{SiK}$  in



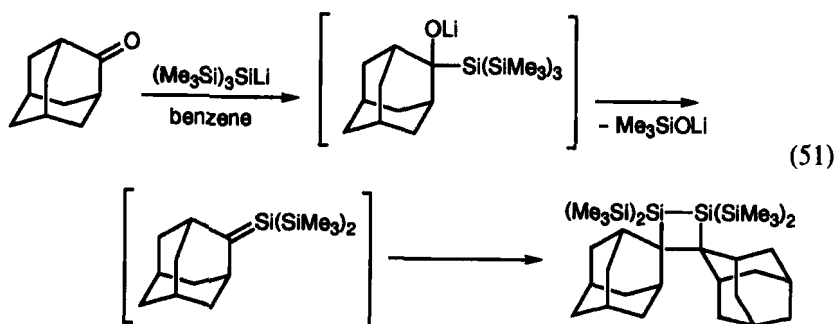
HMPA at 65°C for 3 hours affords the corresponding *trans* and *cis* olefins, respectively. Backside attack of  $\text{Me}_3\text{SiK}$  on the *cis* (and *trans*) epoxides generates the threo- (and erythro-)  $\beta$ -alkoxysilanes, respectively, followed by syn elimination (Peterson elimination) to give the olefin with inverted stereochemistry.



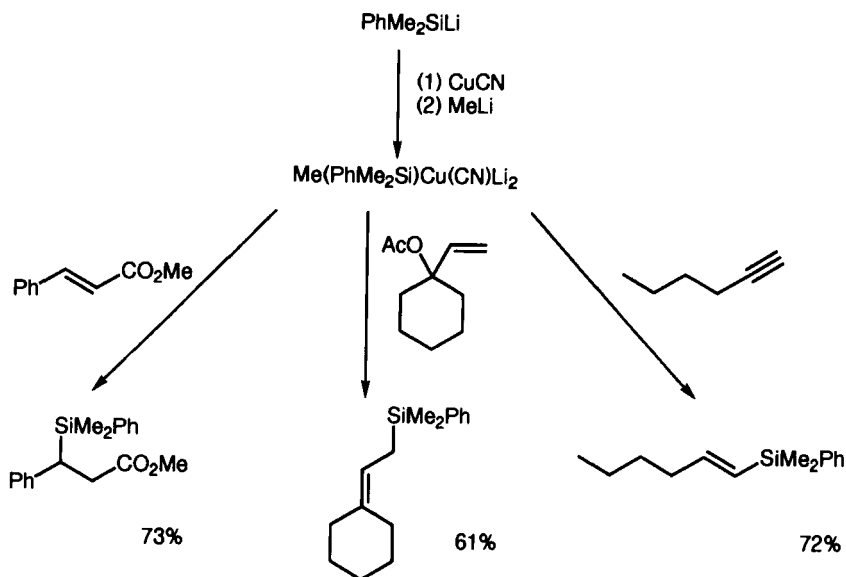
Disilanyllithium  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  also undergoes conjugate addition to an  $\alpha,\beta$ -unsaturated ketone just like  $\text{Me}_3\text{SiLi}$  (68a-c). In comparison with  $\text{Me}_3\text{SiLi}$ ,  $\text{Me}_3\text{SiMe}_2\text{SiLi}$  shows a better stereoselectivity in the addition [Eq. (50)].



Reaction of adamantanone with  $(\text{Me}_3\text{Si})_3\text{SiLi}$  in hexane leads, via a Peterson-type elimination, to the silene, which dimerizes spontaneously to 1,2-disilacyclobutane in 85% yield [Eq. (51)] (98a,b).

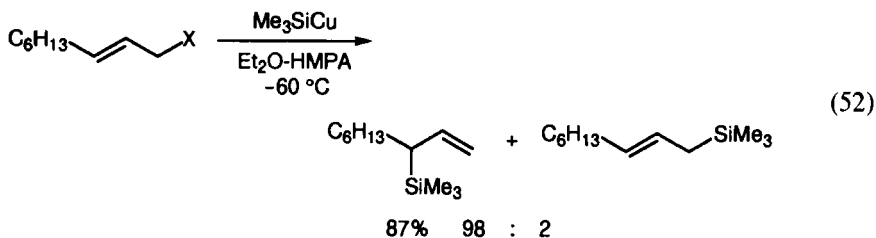


Silyl-copper and silylcuprate reagents are readily prepared by reaction of silyllithiums with copper salts such as  $\text{CuCN}$ ,  $\text{CuI}$ , and  $\text{CuBr}/\text{Me}_2\text{S}$  in ethereal solvent. The silylcuprates  $(\text{PhMe}_2\text{Si})_2\text{CuLi}$ ,  $\text{PhMe}_2\text{SiCu}(\text{CN})\text{Li}$ ,  $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ ,  $\text{Me}(\text{PhMe}_2\text{Si})\text{Cu}(\text{CN})\text{Li}_2$ , and  $(\text{PhMe}_2\text{Si})_3\text{CuLi}_2$



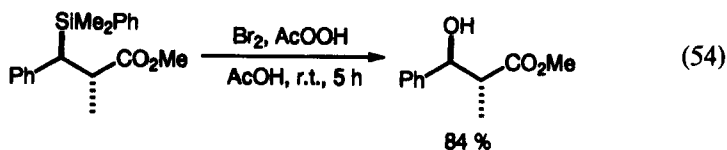
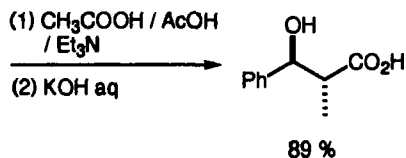
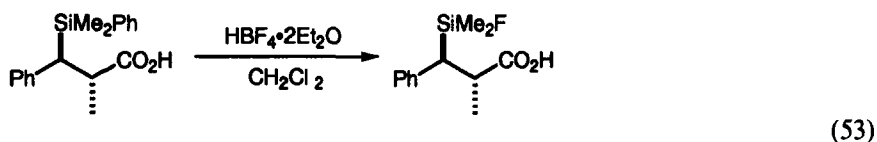
SCHEME 29

have been studied by NMR spectroscopy (see Table I in Section III and Table II in Section IX) (99a–d). Reactions of silylcuprate (PhMe<sub>2</sub>Si)<sub>2</sub>Cu·Li·LiI or (PhMe<sub>2</sub>Si)<sub>2</sub>Cu(CN)Li<sub>2</sub> with various electrophiles have been well investigated (100a–f). Silyl–copper reagents prefer S<sub>N</sub>2' displacement to S<sub>N</sub>2 in the allylic substitution [Eq. (52)] (100a–f). A mixed cuprate, which is prepared from PhMe<sub>2</sub>SiLi, MeLi, and CuCN in an equimolar ratio, transfers specifically the silyl group, not the methyl group, to various electrophiles (Scheme 29).

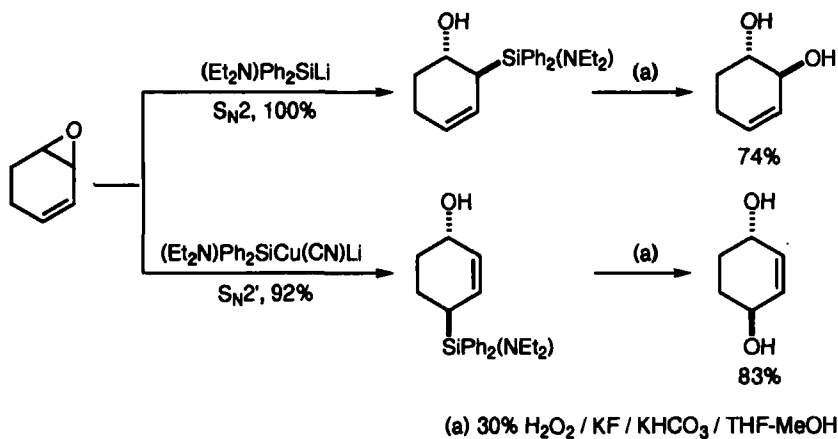


The phenylsilyl group introduced can be converted into the hydroxy group by oxidative cleavage of the Si–C bond, after changing the phenyl group on silicon into fluorine with HBF<sub>4</sub>·Et<sub>2</sub>O. Thus, the PhMe<sub>2</sub>Si<sup>–</sup> anion works as the hydroxy anion HO<sup>–</sup> equivalent [Eq. (53)] (100a–f). A one-

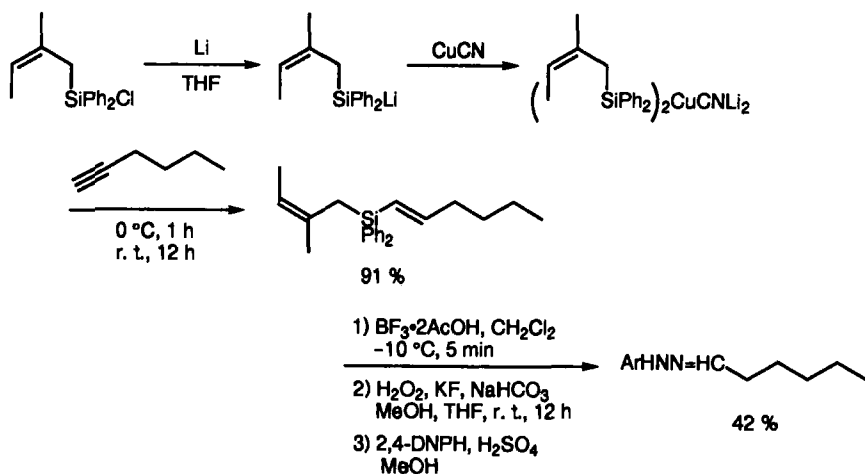
pot procedure is also successful by use of bromine or mercuric acetate in the presence of peracetic acid [Eq. (54)] (100a-f).



(Aminosilyl)lithium,  $(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$  (see also Section V-2), can also be converted into silylcuprate just by mixing with 1 equivalent of  $\text{CuCN}$  in THF (54a-d). The silyllithium undergoes  $\text{S}_{\text{N}}2$  replacement and the silylcuprate does  $\text{S}_{\text{N}}2'$  replacement, with high regio- and stereoselectivity in the allylic substitution reactions (Scheme 30) (54b). The aminosilyl anions serve as a hydroxy anion equivalent in combination with the  $\text{H}_2\text{O}_2$  oxidation of the Si-C bond. These reagents are superior to the phenylsilyl



SCHEME 30



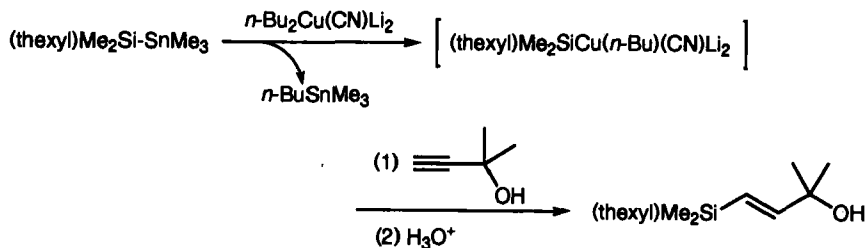
SCHEME 31

analogs,  $\text{PhMe}_2\text{SiLi}$  and  $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ , since no acid treatment is required before the oxidation.

An (allyl)silylcuprate, [(2-methyl-2-butenyl)diphenylsilyl]cuprate, is also a hydroxy anion equivalent. The 2-methyl-2-butenyl group can easily be removed selectively in the presence of other allyl or vinyl groups by protodesilylation under mild conditions (Scheme 31) (13).

Trialkylsilyl higher-order cyanocuprates are prepared directly by transmetallation of silylstannanes with higher-order dibutylcyanocuprates (Scheme 32) (101). In this method, steric bulkiness around silicon is essential for formation of the silylcuprates, so that the *t*-butyl or thexyl group is present on silicon; otherwise, stannyl anion is formed. These reagents undergo typical silyl-cupration reactions, as mentioned earlier.

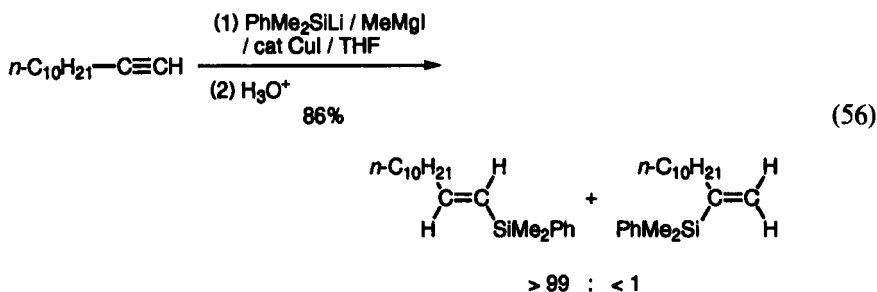
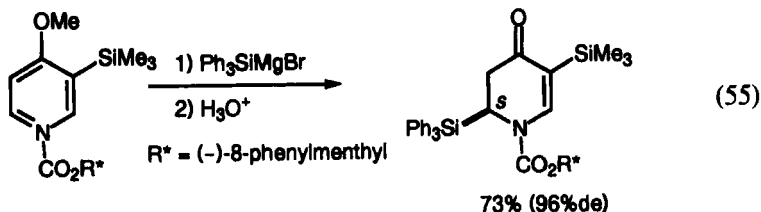
The silylmagnesium reagent  $\text{Ph}_3\text{SiMgBr}$ , which is formed by the addition



thexyl = 1,1,2-trimethylpropyl

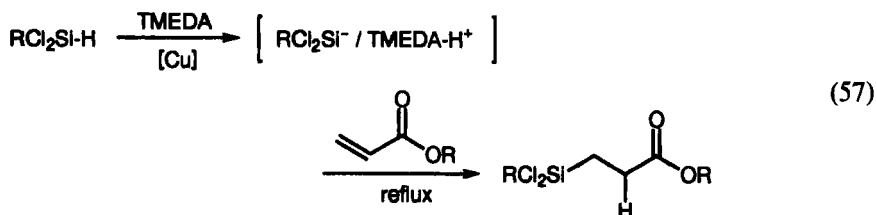
SCHEME 32

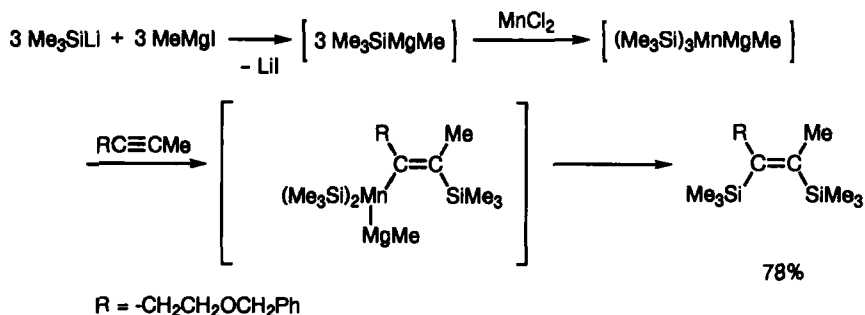
of  $\text{MgBr}_2$  to  $\text{Ph}_3\text{SiLi}$ , undergoes stereoselective addition to chiral 1-acylpyridinium salt to give dihydropyridone [Eq. (55)] (11). The silylmagnesium reagent  $\text{PhMe}_2\text{SiMgMe}$ , prepared from  $\text{PhMe}_2\text{SiLi}$  with Grignard reagent  $\text{MeMgI}$ , undergoes addition smoothly to acetylenes in the presence of a transition-metal catalyst with high regio- and stereoselectivities [Eq. (56)] (102); the silylmagnesium reagent does not cause acetylenic proton-metal exchange with terminal acetylenes.



$\text{Me}_3\text{SiLi}$  or  $\text{PhMe}_2\text{SiLi}$  reacts with  $\text{MeMgI}$  and  $\text{MnCl}_2$  to afford a silylmanganese reagent. These reagents react with acetylenes to form disilylated products (Scheme 33) (103); even the highly crowded tetrasilylethylene can also be prepared.  $\text{MeMgI}$  is essential for the formation of disilylated products; without  $\text{MeMgI}$ , monosilylated products are obtained predominantly.

The trichlorosilyl anion  $[\text{Cl}_3\text{Si}^-/\text{Bu}_3\text{NH}^+]$  (see also Section V-2) is a reductive silylating agent and is useful for some transformations (Scheme 34) (57a–g). A similar species prepared from  $\text{Cl}_3\text{SiH}$  or  $\text{Cl}_2\text{RSiH}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with TMEDA undergoes  $\beta$ -hydrosilylation of acrylates in the presence of a copper salt [Eq. (57)] (58).





SCHEME 33

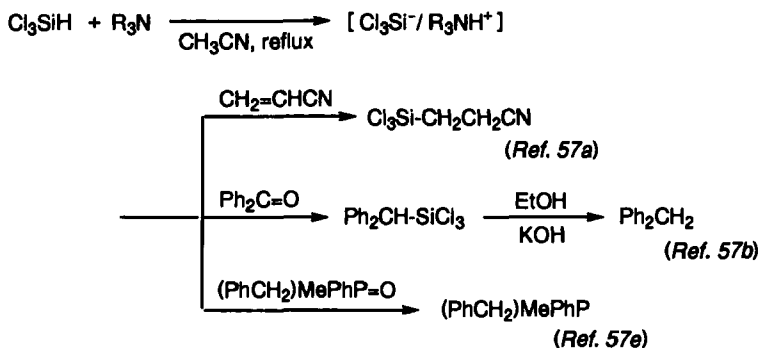
The synthetic applications of  $\text{Me}_3\text{Si}^-/\text{NBu}_4^+$  are illustrated by the reaction with aldehydes and 1,3-dienes (Scheme 35) (39).

## VIII

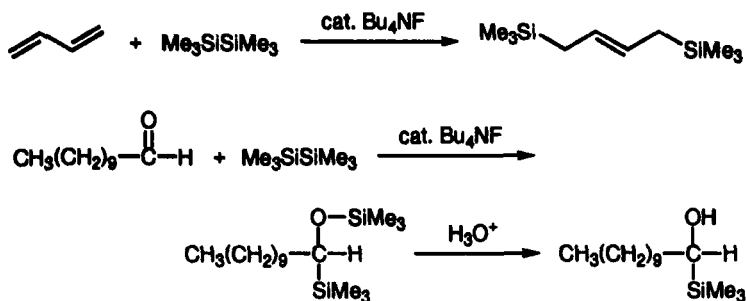
### THEORETICAL STUDY

*Ab initio* calculations for the parent  $\text{H}_3\text{Si}^-$  have been carried out (104), and the effect of second-row substituents on free anions  $\text{XH}_2\text{Si}^-$  ( $\text{X} = \text{BH}_2, \text{CH}_3, \text{NH}_2, \text{OH}, \text{and F}$ ) have been studied (104d,105,106).

The anions were treated using the larger double-zeta basis set for geometry optimizations on both the silyl anions,  $\text{XH}_2\text{Si}^-$ , and their parent silanes,  $\text{XH}_3\text{Si}$ . The following three points may be noted. (1) The stability order has been estimated as follows:  $(\text{CH}_3)_2\text{Si}^- \approx (\text{H}_2\text{N})_2\text{Si}^- < (\text{HO})_2\text{Si}^- = \text{H}_3\text{Si}^- < \text{FH}_2\text{Si}^- < (\text{H}_2\text{B})_2\text{Si}^-$ . (2) The silyl anions,  $\text{XH}_2\text{Si}^-$ , are 50–60



SCHEME 34



SCHEME 35

kcal/mol more stable than the corresponding carbanions,  $\text{XH}_2\text{C}^-$ . (3) The anions are pyramidal, with larger out-of-plane angles than their carbanion analogs, and inversion barriers are high, varying from 34.3 kcal/mol for  $\text{X} = \text{H}$  up to 57.3 kcal/mol for  $\text{X} = \text{F}$ . The calculations agree with the experimental observation that inversion in silyl anions has a lower limit of 24 kcal/mol (24). The out-of-plane angles increase with the electronegativity of the substituent. This is due to  $\pi$ -donation from the substituent (which interacts with the lone pair at the inversion center to produce  $4\pi$  electron destabilization) and  $\sigma$ -withdrawal to the substituent. For the same reason, elongation of the Si-X bond is observed. However, the borylsilyl anion,  $(\text{H}_2\text{B})\text{H}_2\text{Si}^-$ , is planar at both boron and silicon and has a Si-B bond length shorter than in borylsilane,  $\text{H}_2\text{BSiH}_3$ .

Other potentially conjugated anions,  $\text{NCSiH}_2^-$ ,  $\text{O}=\text{CH}-\text{SiH}_2^-$ ,  $\text{HC}\equiv\text{CSiH}_2^-$ , have also been studied (104d, 107a, b). They are also pyramidal at silicon, and their inversion barriers are large, 35.2, 19.9, and 34.3 kcal/mol, respectively.

*Ab initio* calculations on metal-containing silyllithiums and silylsodiums,  $\text{SiLi}_4$ ,  $\text{H}_2\text{SiLi}_2$ ,  $\text{H}_3\text{SiLi}$  and  $\text{H}_2\text{SiNa}_2$ , have also been performed (108a-c). The  $\text{H}_3\text{SiLi}$  species has been calculated with 6-31G\* geometries at the MP4STDQ/6-31G\*\* level, with a correction for zero-point energy (Fig. 7) (108a). The inverted  $\text{SiH}_3\text{Li}$   $\text{C}_{3v}$  structure **A** is 2.4 kcal/mol more stable than the tetrahedral  $\text{C}_{3v}$  isomer **B** because of more favorable electrostatic interactions between Li and H. The best interconversion pathway involves transition structure **C**, which lies 13.5 kcal/mol higher in energy than **A**. The pyramidal inversion barrier of the silyl anion is quite high (24, 108a-c), and the lithium counter-ion wanders over the surface like **C**. Furthermore, the nature of Si-Li bonding has been studied by natural population analysis using natural, localized molecular orbitals. The result indicates that the Si-Li bond is essentially ionic, even in the regular structures like **B**,

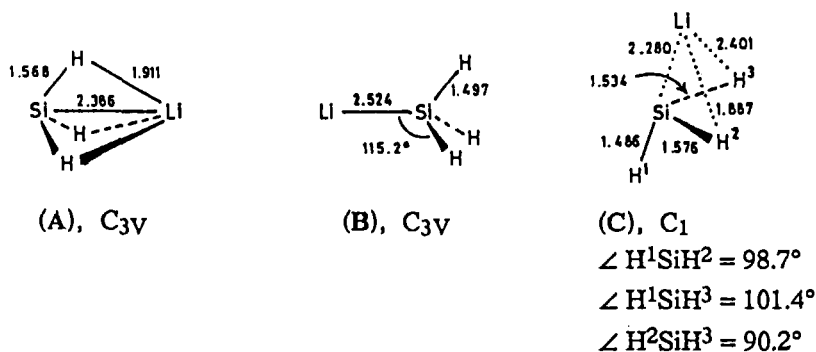


FIG. 7. Three possible geometries for  $H_2SiLi$  (108a). Reprinted with permission from *J. Chem. Soc., Chem. Commun.* **1986**, 1371. Copyright (1986) The Royal Society of Chemistry.

although the partial covalent nature has been confirmed experimentally by NMR spectroscopy (see Section III-B).

Fluorosilyllithium,  $FH_2SiLi$ , is an interesting species, since it has been thought to be a model for silylenoids, analogous to carbenoids. The *ab initio* calculation has been performed with STO-3G and 3-21G (109). The two most stable forms are suggested to be the  $H_2SiLi^+F^-$  ion pair and the  $H_2Si:FLi$  complex (Fig. 8). It is interesting that lithium interacts with fluorine in both forms. In  $H_2SiLi^+F^-$ , lithium substitution causes effective stabilization of  $SiH_2^+$  (56.8 kcal/mol at STO-3G for  $H_2SiLi^+$ ), and results in the weakening of the strong Si-F bond. These results suggest that  $SiH_2LiF$  exhibits electrophilicity due to the cationic silicon center. Thus, silylenoid nature appears in  $SiH_2LiF$ .

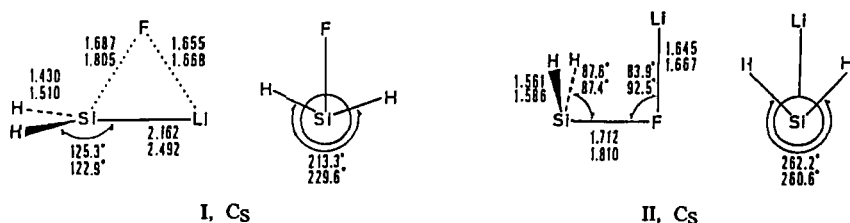


FIG. 8. Two stable geometries for  $FH_2SiLi$  optimized by STO-3G (upper) and 3-21G (lower) levels. Bond lengths are in angstroms and bond angles in degrees (110). Reprinted with permission from *J. Organomet. Chem.* **1980**, 191, 347. Copyright (1980) Elsevier Science S. A.



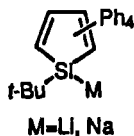
## IX

 **$^{29}\text{Si}$  NMR DATA OF SILYL ANIONS**

$^{29}\text{Si}$  NMR chemical shifts and coupling constants are compiled in Table II.

TABLE II  
 $^{29}\text{Si}$  NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SILYL ANIONS

Compound	$\delta$ (ppm)	$^1J$ (Hz)	Temp.	Solvent	Reference
$\text{Ph}_3\text{SiLi}$	-30.0		room temp.	THF	(20)
	-9.0		295 K	THF	(19b)
	-9.3	t 17 [ $^{29}\text{Si}$ , $^6\text{Li}$ ]	173 K	MTHF	(19b)
	9.28	q 45 [ $^{29}\text{Si}$ , $^7\text{Li}$ ]	193 K	$\text{C}_7\text{D}_8$	(22)
$\text{Ph}_2\text{MeSiLi}$	-20.5		room temp.	THF	(20)
	-23.1	t 15 [ $^{29}\text{Si}$ , $^6\text{Li}$ ]	158 K	THF	(19b)
$\text{PhMe}_2\text{SiLi}$	-22.1		room temp.	THF	(20)
	-29.1	t 18 [ $^{29}\text{Si}$ , $^6\text{Li}$ ]	173 K	THF	(19b)
$(\text{PhMe}_2\text{Si})_2\text{CuLi}$	-24.4		223 K	THF	(99a-d)
$\text{PhMe}_2\text{SiCu}(\text{CN})\text{Li}$	-25.5		223 K	THF	(99a-d)
$(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$	-24.4		223 K	THF	(99a-d)
$\text{Me}(\text{PhMe}_2\text{Si})\text{Cu}(\text{CN})\text{Li}_2$	-20.6		223 K	THF	(99a-d)
$(\text{PhMe}_2\text{Si})_3\text{CuLi}_2$	-18.9		223 K	THF	(99a-d)
$\text{Me}_3\text{SiLi}$	-32.8	t 21.1 [ $^{29}\text{Si}$ , $^6\text{Li}$ ]	223 K	$\text{THF-d}_8$	(70)
$\text{Me}_3\text{SiK}$	-34.4		room temp.	HMPA	(20)
$\text{H}_3\text{SiK}$	-165.0	q 75 [ $^{29}\text{Si}$ , $^1\text{H}$ ]	room temp.	HMPA	(46)
$\text{Cl}_3\text{SiLi}$	30.9		room temp.	THF	(56)
$\text{HMe}_2\text{SiLi}$	-71.78	d 101 [ $^{29}\text{Si}$ , $^1\text{H}$ ]	293 K	$\text{C}_6\text{D}_6$	(52)
$(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$	19.34		273 K	THF	(54a)
$\left[ (\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{O}^-)\text{Mes} \right] \text{Li}^+$	-59.9		233 K	THF	(60)



$\text{M} = \text{Li}$	25.10	room temp.	$\text{THF-d}_8$	(64a)
$\text{M} = \text{Na}$	26.12	room temp.	$\text{THF-d}_8$	(64a)

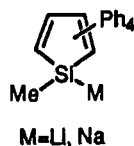
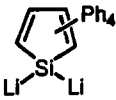
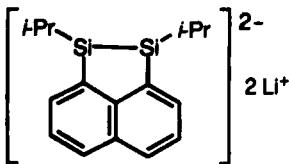


TABLE II (continued)

Compound	$\delta$ (ppm)	$^1J$ (Hz)	Temp.	Solvent	Reference
M = Li	-19.29		room temp.	THF-d <sub>8</sub>	(64b)
M = Na	-33.51		room temp.	THF-d <sub>8</sub>	(64b)
					
	68.54		room temp.	THF-d <sub>8</sub>	(65b)
PhMe <sub>2</sub> SiMe <sub>2</sub> SiLi	-69.8	31[ <sup>29</sup> Si, <sup>29</sup> Si]	room temp.	THF-d <sub>8</sub>	(28)
Me <sub>3</sub> SiMe <sub>2</sub> SiLi	-74.9	t 18.8[ <sup>29</sup> Si, <sup>6</sup> Li] 19.1[ <sup>29</sup> Si, <sup>29</sup> Si]	180 K	THF-d <sub>8</sub>	(70)
					
Me <sub>3</sub> SiMe <sub>2</sub> SiMe <sub>2</sub> SiLi	-1.24	q 43.5[ <sup>29</sup> Si, <sup>7</sup> Li]	173 K	THF-d <sub>8</sub>	(71)
(Me <sub>3</sub> Si) <sub>2</sub> MeSiLi	-62.7	t 18.6[ <sup>29</sup> Si, <sup>6</sup> Li]	180 K	THF-d <sub>8</sub>	(70)
(Me <sub>3</sub> Si) <sub>3</sub> SiLi	-133.8		180 K	THF-d <sub>8</sub>	(70)
[(Me <sub>3</sub> Si) <sub>3</sub> Si] <sub>2</sub> Cu <sub>2</sub> Br](Li·3THF)	-185.4		room temp.	C <sub>6</sub> D <sub>6</sub>	(75)
[(Me <sub>3</sub> Si) <sub>3</sub> Si] <sub>2</sub> M	-129.88		room temp.	C <sub>6</sub> D <sub>6</sub>	(76c)
M = Zn	-123.9		296 K	C <sub>6</sub> D <sub>6</sub>	(79a)
M = Cd	-109.2		296 K	C <sub>6</sub> D <sub>6</sub>	(79a)
M = Hg	-54.5		296 K	C <sub>6</sub> D <sub>6</sub>	(79a)
(Me <sub>3</sub> Sn) <sub>3</sub> SiLi	-122.0	239[ <sup>29</sup> Si, Sn]	296 K	C <sub>6</sub> D <sub>6</sub>	(81b)
Li(Ph <sub>2</sub> Si) <sub>4</sub> Li	-28.54		303 K	THF	(85b)
Me <sub>11</sub> Si <sub>6</sub> Li	-108.1		310 K	HMPA	(86)

## X

## LIST OF SILYL ANIONS

Known silyl anions are summarized, together with references.

*Arylsilyl Anions*

Ph<sub>3</sub>SiLi (3,6,7,9a); Ph<sub>3</sub>SiNa (6); Ph<sub>3</sub>SiK (5,8); Ph<sub>3</sub>SiRb (3); Ph<sub>3</sub>SiCs (3)  
 Ph<sub>3</sub>SiMgBr (9-11); (Ph<sub>3</sub>Si)<sub>2</sub>Hg (12); (*o*-Tolyl)<sub>3</sub>SiLi (3); [Ph<sub>3</sub>Si<sup>-</sup>/*n*-Bu<sub>4</sub>N<sup>+</sup>]  
 (39)  
 Ph<sub>2</sub>MeSiLi (26); Ph<sub>2</sub>MeSiK (19a); Ph<sub>2</sub>(*t*-Bu)SiLi (74); Ph<sub>2</sub>(*t*-Bu)SiK (110);  
 Ph<sub>2</sub>(*n*-Bu)SiLi (54d)



( $\alpha$ -Naph)PhMeSi\*Li (9a,b); ( $\alpha$ -Naph)PhMeSi\*MgBr (9a,b); [( $\alpha$ -Naph)-  
 PhMeSi\*]<sub>2</sub>Hg (16)  
 PhMe<sub>2</sub>SiLi (26); PhMe<sub>2</sub>SiK (19a); [(PhMe<sub>2</sub>Si)<sub>4</sub>Hg]Li<sub>2</sub> (33b)  
 PhEt<sub>2</sub>SiLi (112); Ph(*i*-Pr)<sub>2</sub>SiLi (24)  
 Ph(PhCH<sub>2</sub>)<sub>2</sub>SiLi (24); (*neo*-C<sub>3</sub>H<sub>11</sub>)PhMeSi\*Li (15)  
 (PhMe<sub>2</sub>Si)<sub>2</sub>CuLi (99a-d, 100b); PhMe<sub>2</sub>SiCu(CN)Li (99a-d)  
 (PhMe<sub>2</sub>Si)<sub>2</sub>Cu(CN)Li<sub>2</sub> (99a-d, 100b); Me(PhMe<sub>2</sub>Si)Cu(CN)Li<sub>2</sub> (99a-d,  
 100b); (PhMe<sub>2</sub>Si)<sub>3</sub>CuLi<sub>2</sub> (99a-d)  
 PhMe<sub>2</sub>SiLi/MeMgI (102); PhMe<sub>2</sub>SiLi/ZnBr<sub>2</sub> (102)  
 [PhMe<sub>2</sub>Si<sup>-</sup>/*n*-Bu<sub>4</sub>N<sup>+</sup>] (39)

*Alkylsilyl Anions*

Me<sub>3</sub>SiLi (29,34b,70); Me<sub>3</sub>SiNa (8,30a,b); Me<sub>3</sub>SiK (8,30a,b,31);  
 (Me<sub>3</sub>Si)<sub>2</sub>Mg (32,36)  
 (Me<sub>3</sub>Si)<sub>2</sub>Hg (35); (Me<sub>3</sub>Si)<sub>2</sub>Zn (38a-c); (Me<sub>3</sub>Si)<sub>2</sub>Cd (38a-c)  
 (Me<sub>3</sub>Si)<sub>3</sub>HgLi (33a); (Me<sub>3</sub>Si)<sub>4</sub>HgLi<sub>2</sub> (33a,b); (Me<sub>3</sub>Si)<sub>4</sub>HgNa<sub>2</sub> (33a);  
 (Me<sub>3</sub>Si)<sub>4</sub>HgK<sub>2</sub> (33a)  
 (Me<sub>2</sub>SiCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>Hg<sub>2</sub> (112)  
 Et<sub>3</sub>SiLi (34b); Et<sub>3</sub>SiNa (34b); Et<sub>3</sub>SiK (8,34a,b); (Et<sub>3</sub>Si)<sub>2</sub>Hg (34a,b)  
*t*-Bu<sub>3</sub>SiLi (40); *t*-Bu<sub>3</sub>SiNa (40); *t*-Bu<sub>3</sub>SiK (40); *t*-Bu<sub>3</sub>SiRb (40); *t*-Bu<sub>3</sub>SiCs  
 (40)  
*t*-Bu<sub>3</sub>SiMgBr (40); (*t*-Bu<sub>3</sub>Si)<sub>2</sub>Cd (38a-c)  
 (Me<sub>3</sub>Si)<sub>2</sub>CuLi (99b); Me<sub>3</sub>SiLi/CuI/Me<sub>2</sub>S (100f); Me<sub>3</sub>SiLi/MeMgI/MnCl<sub>2</sub>  
 (103)  
*t*-BuMe<sub>2</sub>SiCu(*n*-Bu)(CN)Li<sub>2</sub> (101); (Thexyl)Me<sub>2</sub>SiCu(*n*-Bu)(CN)Li<sub>2</sub> (101)  
 [Me<sub>3</sub>Si<sup>-</sup>/*n*-Bu<sub>4</sub>N<sup>+</sup>] (39)

*Functionalized Silyl Anions*

$\text{SiLi}_4$  (49);  $\text{H}_3\text{SiK}$  (44)

$\text{HPh}_2\text{SiLi}$  (54e,56);  $\text{HMes}_2\text{SiLi}$  (51–53)

$\text{Cl}_3\text{SiLi}$  (50);  $\text{Cl}_3\text{Si}^-[\text{R}_3\text{NH}]^+$  (57a–g)

$\text{Cl}_3\text{Si}^-[\text{TMEDA-H}]^+$  (58);  $\text{Cl}_2\text{PhSi}^-[\text{TMEDA-H}]^+$  (58);

$\text{Cl}_2\text{MeSi}^-[\text{TMEDA-H}]^+$  (58)

$(\text{Et}_2\text{N})\text{Ph}_2\text{SiLi}$  (54a,e);  $(\text{Et}_2\text{N})_2\text{PhSiLi}$  (54a);  $(\text{Et}_2\text{N})\text{PhMeSiLi}$  (54a)

$(\text{Et}_2\text{N})\text{Ph}_2\text{SiMg-}i\text{-Pr}$  (54b);  $(\text{Et}_2\text{N})\text{PhMeSiMg-}i\text{-Pr}$  (54b)

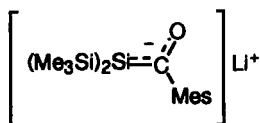
$(\text{Et}_2\text{N})\text{Ph}_2\text{SiCu(CN)Li}$  (54a);  $(\text{Et}_2\text{N})_2\text{PhSiCu(CN)Li}$  (54b)

$(t\text{-BuO})\text{Ph}_2\text{SiLi}$  (54d,e);  $(i\text{-PrO})\text{Ph}_2\text{SiLi}$  (54e);  $(\text{MeO})\text{Ph}_2\text{SiLi}$  (54e);

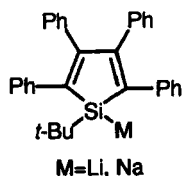
$(t\text{-BuO})_2\text{PhSiLi}$  (54e,f);  $(\text{CH}_2=\text{CH-Me}_2\text{C-O-})\text{Ph}_2\text{SiLi}$  (54g);

$(\text{CH}_2=\text{CH-Et}_2\text{C-O-})(p\text{-tolyl})_2\text{SiLi}$  (54f)

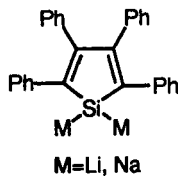
$(\text{MeO})\text{Me}_2\text{SiNa}$  (55a);  $(\text{MeO})_2\text{MeSiNa}$  (55a)



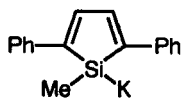
(60)



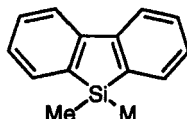
(64)



(65)



(14)



(14, 66, 67)

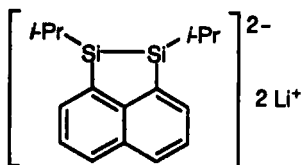
*Disilanyl Anions*

$\text{H}_3\text{SiH}_2\text{SiK}$  (44);  $(\text{H}_3\text{Si})_2\text{HSiK}$  (44);  $(\text{H}_3\text{Si})_3\text{SiK}$  (44)

$\text{Me}_3\text{SiMe}_2\text{SiLi}$  (68a–c,70);  $\text{Me}_3\text{SiMe}_2\text{Si}^-[\text{Bu}_4\text{N}]^+$  (39)

$\text{Me}_3\text{SiPh}_2\text{SiLi}$  (69);  $\text{Me}_3\text{SiMes}_2\text{SiLi}$  (69);  $\text{PhMe}_2\text{SiMe}_2\text{SiLi}$  (28)

$\text{Ph}_3\text{SiPh}_2\text{SiLi}$  (113);  $\text{Ph}_3\text{SiPh}_2\text{SiK}$  (114);  $(t\text{-BuO})\text{Ph}_2\text{SiPh}_2\text{SiLi}$  (54d)



(72)

**Polysilanyl Anions**

(Me<sub>3</sub>Si)<sub>3</sub>SiLi (73–77, 80b, c, 98b); (HMe<sub>2</sub>Si)<sub>3</sub>SiLi (73a–c); (Me<sub>3</sub>Si)<sub>2</sub>MeSiLi (70, 73a–c)

(Me<sub>3</sub>Si)<sub>2</sub>SiLi<sub>2</sub> (82)

(Me<sub>3</sub>Si)<sub>3</sub>SiK (79b); (Me<sub>3</sub>Si)<sub>3</sub>SiRb (79b); (Me<sub>3</sub>Si)<sub>3</sub>SiCs (79b)

[(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Zn (79a); [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Cd (79a); [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Hg (79a)

[(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Cu<sub>5</sub>Cl<sub>4</sub>[(Li·4THF) (80b); [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Cu<sub>2</sub>Br[(Li·3THF) (80c)

(Me<sub>3</sub>Sn)<sub>3</sub>SiLi (81a, b)

[(R<sub>3</sub>Si)<sub>3</sub>SiSi(SiR<sub>3</sub>)<sub>2</sub>Li (74); Li[(R<sub>3</sub>Si)<sub>2</sub>SiSi(SiR<sub>3</sub>)<sub>2</sub>Li (72, 74);

K[(R<sub>3</sub>Si)<sub>2</sub>SiSi(SiR<sub>3</sub>)<sub>2</sub>]K (72)

LiPh<sub>2</sub>Si(Ph<sub>2</sub>Si)<sub>2</sub>Ph<sub>2</sub>SiLi (84b, 85b); LiPh<sub>2</sub>Si(Ph<sub>2</sub>Si)<sub>3</sub>Ph<sub>2</sub>SiLi (84c)

Me<sub>3</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiLi (70); (PhMe<sub>2</sub>Si)<sub>2</sub>MeSiLi (70)

cyclo-Me<sub>11</sub>Si<sub>6</sub>-M (M = Li, Na, K) (86)

cyclo-Me<sub>9</sub>Si<sub>5</sub>-K (87); (cyclo-Me<sub>9</sub>Si<sub>5</sub>)<sub>2</sub>Hg (87)

**Model for Calculation**

H<sub>3</sub>Si<sup>-</sup> (104–106); (H<sub>2</sub>B)H<sub>2</sub>Si<sup>-</sup> (105, 106); (H<sub>3</sub>C)H<sub>2</sub>Si<sup>-</sup> (105, 106);

(H<sub>2</sub>N)H<sub>2</sub>Si<sup>-</sup> (105, 106)

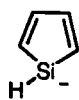
(HO)H<sub>2</sub>Si<sup>-</sup> (105, 106); FH<sub>2</sub>Si<sup>-</sup> (105, 106)

(N≡C—)H<sub>2</sub>Si<sup>-</sup> (107a); (O=CH—)H<sub>2</sub>Si<sup>-</sup> (107a); (HC≡C—)H<sub>2</sub>Si<sup>-</sup> (107b);

H<sub>3</sub>SiH<sub>2</sub>Si<sup>-</sup> (104d)

SiLi<sub>4</sub> (108b); H<sub>2</sub>SiLi<sub>2</sub> (108b); H<sub>2</sub>SiNa<sub>2</sub> (108b); H<sub>3</sub>SiLi (108b, 108d)

FH<sub>2</sub>SiLi (109); (H<sub>3</sub>Si)<sub>2</sub>SiLi(COCH<sub>3</sub>) (60)



(62, 63)

## XI

## CONCLUDING REMARKS

The chemistry of silyl anions has been surveyed. While silyl anion chemistry has been developing steadily and rapidly in recent years, it still lags far behind carbanion chemistry in terms of the number and kind of anions so far studied. When compared to carbanion chemistry, however, silyl anion chemistry has intriguing and unique features, such as softer nucleophilicity, preference for monomeric structure in solution, high inversion barrier of pyramidal structure, generation of 1,1- and 1, $\omega$ -dianions, and redistribution reactions of oligo- and polysilanes with silyl anions. More extensive studies are expected to disclose other properties, reactivities, and utilities of silyl anions. Studies of silyl anions, however, sometimes encounter difficulty in preparation of silyl anions with various kinds of substituents, especially functional groups. Further development thus greatly depends on the exploitation of new methodologies for preparation of silyl anions.

## REFERENCES

- (1) Previous reviews include (a) Wittenberg, D.; Gilman, H. *Q. Rev.* **1969**, *13*, 116; (b) Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 283; (c) Wiberg, E.; Stecher, O.; Andrascheck, H. J.; Kreuzbichler, L.; Staude, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 507; (d) Fujita, M.; Hiyama, T. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 293; (e) Colvin, E. W. "Silicon Organic Synthesis"; Butterworth: London, 1981; pp. 134–140; (f) Fleming, I. In "Comprehensive Organic Chemistry"; Barton, E.; Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, pp. 664–669; for theoretical studies, see (g) Apeloig, Y. In "The Chemistry of Organic Silicon Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1989; p. 201; (h) Lambert, J. B.; Schultz, W. J., Jr. In "The Chemistry of Organic Silicon Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 16, pp. 1007–1010; for structural studies, see (i) Sheldrick, W. S. In "The Chemistry of Organic Silicon Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1989; p. 268.
- (2) Tilley, T. D. In "The Chemistry of Organosilicon Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 24, pp. 1415–1477; Silylcuprates and silylcopper: Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005; Transition metal catalyzed silylmatalation: Oshima, K. In "Advances in Metal-Organic Chemistry"; Liebeskind, L. S., Ed.; JAI Press: London, 1991, Vol. 2, pp. 101–141.
- (3) George, M. V.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 404.
- (4) Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 6129.
- (5) Gilman, H.; Wu, T. C. *J. Am. Chem. Soc.* **1951**, *73*, 4031.
- (6) Brook, A. G.; Gilman, H. *J. Am. Chem. Soc.* **1954**, *76*, 278.
- (7) Benkeser, R. A.; Severson, R. G. *J. Am. Chem. Soc.* **1951**, *73*, 1424.
- (8) Corriu, R. J. P.; Guérin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168.

- (9a) Colomer, E.; Corriu, R. J. P. *J. Chem. Soc., Chem. Commun.* **1976**, 176.  
(9b) Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1977**, 133, 159.  
(10) Selin, T. G.; West, R. *Tetrahedron* **1959**, 5, 97.  
(11) Comins, D. L.; Killpack, M. O. *J. Am. Chem. Soc.* **1992**, 114, 10972.  
(12) Jackson, R. A. *Chem. Commun.* **1966**, 827.  
(13) Fleming, I.; Winter, S. B. D. *Tetrahedron Lett.* **1993**, 34, 7287.  
(14) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973.  
(15) Sommer, L. H.; Mason, R. J. *Am. Chem. Soc.* **1965**, 87, 1619.  
(16) Eaborn, C.; Jackson, R. A.; Rahman, M. T. *J. Organomet. Chem.* **1972**, 34, 7; Eaborn, C.; Jackson, R. A.; Tune, D. J.; Walton, D. R. M. *ibid.* **1973**, 63, 85.  
(17) Brefort, J. L.; Corriu, R. J. P.; Guérin, C.; Henner, B. *J. Organomet. Chem.* **1989**, 370, 9.  
(18) Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, 108, 3139.  
(19a) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, U. *J. Am. Chem. Soc.* **1985**, 107, 303.  
(19b) Edlund, U.; Lejon, T.; Venkatachalam, T. K.; Buncel, E. *J. Am. Chem. Soc.* **1985**, 107, 6408.  
(19c) Rakita, P. E.; Srebro, J. P.; Worsham, L. S. *J. Organomet. Chem.* **1976**, 104, 27.  
(20) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, 102, 6989.  
(21) Waack, R.; Doran, M. A. *Chem. Ind. (London)* **1965**, 563; Evans, A. G.; Hamid, M. A.; Rees, N. H. *J. Chem. Soc. B* **1971**, 1110.  
(22) Davis, H. V. R.; Olmstead, M. M.; Ruhlandt-Senge, K.; Power, P. P. *J. Organomet. Chem.* **1993**, 462, 1.  
(23) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, 341, 1.  
(24) Lambert, J. B.; Urdaneta-Pérez, M. *J. Am. Chem. Soc.* **1978**, 100, 157.  
(25) Hayashi, T.; Okamoto, Y.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1072.  
(26) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, 80, 608.  
(27) Gilman, H.; Lichtenwalter, G. D.; Wittenberg, D. *J. Am. Chem. Soc.* **1959**, 81, 5320.  
(28) Ruehl, K. E.; Davis, M. E.; Matyjaszewski, K. *Organometallics* **1992**, 11, 788.  
(29) Still, W. C. *J. Org. Chem.* **1976**, 41, 3063.  
(30a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 19, 1511.  
(30b) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, 92, C46.  
(31) Shippey, M. A.; Dervan, P. B. *J. Org. Chem.* **1977**, 42, 2654.  
(32) Eaborn, C.; Jackson, R. A.; Walsingham, R. W. *J. Chem. Soc. C* **1967**, 2188.  
(33a) Schaaf, T. F.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, 91, 4327.  
(33b) Isley, W. H.; Albright, M. J.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1980**, 19, 3577.  
(34a) Vyazankin, N. S.; Razuvaev, G. A.; Gladyshev, E. N.; Korneva, S. P. *J. Organomet. Chem.* **1967**, 7, 353.  
(34b) Gladyshev, E. N.; Fedorova, E. A.; Yuntala, L. O.; Razuvaev, G. A.; Vyazankin, N. S. *J. Organomet. Chem.* **1975**, 96, 169.  
(35) Hengge, E.; Holtschmidt, N. *J. Organomet. Chem.* **1968**, 12, P5.  
(36) Glaggett, A. R.; Ilsley, W. H.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1977**, 99, 1797.  
(37) Rösch, L. *J. Organomet. Chem.* **1976**, 121, C15.  
(38a) Rösch, L.; Müller, H. *Angew. Chem., Int. Ed. Engl.* **1976**, 15, 620.  
(38b) Rösch, L.; Altnau, G. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 60.  
(38c) Rösch, L.; Altnau, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, 35, 195.  
(39) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, 48, 912; Hiyama, T.; Obayashi, M. *Tetrahedron Lett.* **1983**, 24, 4109; Hiyama, T.; Obayashi, M.; Sawahata, M. *ibid.*, 4113.

- (40) Wiberg, N. In "Frontiers of Organosilicon Chemistry"; Bassindale, A. R.; Gaspar, P. P., Eds.; Royal Society of Chemistry: London, 1991; pp. 263–270; Wiberg, N.; Fischer, G.; Karampatses, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 59; Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *ibid.* **1986**, *25*, 79; Wiberg, N.; Schurz, K. *J. Organomet. Chem.* **1988**, *341*, 145.
- (41) Schaaf, T. F.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 7593; Ilsley, W. H.; Schaaf, T. F.; Glick, M. D.; Oliver, J. P. *ibid.* **1980**, *102*, 3769.
- (42) Teclé, B.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875.
- (43) Bleckmann, P.; Soliman, M.; Reuter, K.; Neumann, W. P. *J. Organomet. Chem.* **1976**, *108*, C18.
- (44) Ring, M. A.; Ritter, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 802; *J. Phys. Chem.* **1961**, *65*, 182.
- (45) Amberger, E.; Mühlhofer, E. *J. Organomet. Chem.* **1968**, *12*, 55.
- (46) Bürger, H.; Eujen, R.; Marsmann, H. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29B*, 149.
- (47) Mundt, O.; Becker, G.; Hartmann, H. M.; Schwarz, W. Z. *Anorg. Allg. Chem.* **1989**, *572*, 75.
- (48) Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522.
- (49) Morrison, J. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 2972.
- (50) Gilman, H.; Steudel, W. *Chem. Ind. (London)* **1959**, 1094.
- (51) Weidenbruch, M.; Kramer, K.; von Schnering, H. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 601.
- (52) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324.
- (53) Stüger, H. *J. Organomet. Chem.* **1993**, *458*, 1.
- (54a) Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989. The  $^{29}\text{Si}$  NMR data have been corrected by reinvestigation (1994).
- (54b) Tamao, K.; Kawachi, A.; Ito, Y. "Proceedings of the 10th International Symposium on Organosilicon Chemistry, Poznan, Poland, **1993** (in press).
- (54c) Tamao, K.; Kawachi, A.; Ito, Y. *Organometallics* **1993**, *12*, 580.
- (54d) Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 818.
- (54e) Tamao, K.; Kawachi, A. *Organometallics* **1995**, in press.
- (54f) Tamao, K. "28th Organosilicon Symposium, 1995, Gainesville, Florida, USA," Abstracts, p. A-4.
- (54g) Tamao, K.; Kawachi, A. "6th International Kyoto Conference on New Aspects of Organic Chemistry, 1994, Kyoto, Japan," Abstracts, p. 143.
- (55a) Watanabe, H.; Higuchi, K.; Kobayashi, M.; Hara, M.; Koike, Y.; Kitahara, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 534.
- (55b) Watanabe, H.; Higuchi, K.; Goto, T.; Muraoka, T.; Inose, J.; Kageyama, M.; Iizuka, Y.; Nozaki, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *218*, 27.
- (56) Oehme, H.; Weiss, H. *J. Organomet. Chem.* **1987**, *319*, C16.
- (57a) Nozakura, S.; Konotune, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 322.
- (57b) Benkeser, R. A.; Foley, K. M.; Gaul, J. M.; Li, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 3232.
- (57c) Li, G. S.; Ehler, D. F.; Benkeser, R. A. *Org. Synth., Collect. Vol.* **1988**, *6*, 747.
- (57d) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *4*, 94.
- (57e) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.
- (57f) Benkeser, R. A.; Foley, K. M.; Grutsner, J. B.; Smith, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 697.
- (57g) Bernstein, S. C. *J. Am. Chem. Soc.* **1970**, *92*, 699.
- (58) Boudjouk, P.; Kloos, S.; Amirhithi, B. *J. Organomet. Chem.* **1993**, *443*, C41.
- (59) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson,



- K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355; Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *ibid.* **1991**, *30*, 902; Corriu, R.; Lanneau, G.; Priou, C.; Soulaïrol, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. J. *J. Organomet. Chem.* **1994**, *466*, 55.
- (60) Ohshita, J.; Masaoka, Y.; Masaoka, S.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *J. Organomet. Chem.* (in press).
- (61) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.
- (62) Damewood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5028.
- (63) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.
- (64a) Hong, J. H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883.
- (64b) Sohn, H.; Bankwitz, U.; Powell, D. R.; West, R. "28th Organosilicon Symposium, 1995, Gainesville, Florida, USA"; Abstracts, p. 68.
- (65a) Joo, W. C.; Hong, J. H.; Choi, S. B.; Son, H. E. *J. Organomet. Chem.* **1990**, *391*, 27.
- (65b) Hong, J. H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387.
- (65c) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. "28th Organosilicon Symposium, 1995, Gainesville, Florida, USA," Abstracts, p. 65.
- (65d) Sohn, H.; Bankwitz, U.; Calabrese, J.; West, R. "28th Organosilicon Symposium, 1995, Gainesville, Florida, USA," Abstracts, p. 69.
- (66) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3243.
- (67) Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. *Organometallics* **1983**, *2*, 351.
- (68a) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.
- (68b) Hwu, J. R.; Wetzol, J. M.; Lee, J. S.; Butcher, R. J. *J. Organomet. Chem.* **1993**, *453*, 21.
- (68c) Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99.
- (69) Brook, A. G.; Baumegeger, A.; Lough, A. J. *Organometallics* **1992**, *11*, 310.
- (70) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195.
- (71) Wakahara, T.; Akasaka, T.; Ando, W. *Organometallics* **1994**, *13*, 4683.
- (72) Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. "10th International Symposium on Organosilicon Chemistry, 1993, Poznań, Poland"; Abstracts, p. 189; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.
- (73a) Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848.
- (73b) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91.
- (73c) Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67.
- (74) Smith, C. M.; Lickiss, P. D. "10th International Symposium on Organosilicon Chemistry, 1993, Poznań, Poland"; Abstracts, p. 263.
- (75) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.
- (76) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694.
- (77) Becker, G.; Hartmann, H. M.; Münch, A.; Riffel, H. Z. *Anorg. Allg. Chem.* **1985**, *530*, 29.
- (78) Klinkhammer, K. W.; Schwarz, W. "10th International Symposium on Organosilicon Chemistry, 1993, Poznań, Poland"; Abstracts, p. 191.
- (79a) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1987**, *26*, 2106.
- (79b) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681.
- (80a) Mallela, S. P.; Bernal, I.; Geanangel, R. A. *Inorg. Chem.* **1992**, *31*, 1626.
- (80b) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 121.
- (80c) Heine, A.; Herbst-Irmer, R.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1993**, 1729.
- (81a) Biffar, W.; Gasparis-Ebeling, T.; Nöth, H.; Storch, W.; Wrackmeyer, B. *J. Magn. Reson.* **1981**, *44*, 54.

- (81b) Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1990**, *29*, 4051.
- (82) Mehrotra, S. K.; Kawa, H.; Baran, J. R., Jr.; Ludvig, M. M.; Lagow, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 9003.
- (83) Wittenberg, D.; George, M. V.; Gilman, H. *J. Am. Chem. Soc.* **1959**, *81*, 4812.
- (84a) Jarvie, A. W. P.; Gilman, H. *J. Org. Chem.* **1961**, *26*, 1999.
- (84b) Jarvie, A. W.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1961**, *83*, 1921.
- (84c) Gilman, H.; Tomasi, R. A. *Chem. Ind. (London)* **1963**, 954.
- (85a) Hengge, E.; Wolfer, D. *J. Organomet. Chem.* **1974**, *66*, 413.
- (85b) Becker, G.; Hartmann, H. M.; Hengge, E.; Schrank, F. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63.
- (86) Allred, A. L.; Smart, R. T.; Beek, D. A. V., Jr. *Organometallics* **1992**, *11*, 4225.
- (87) Hengge, E.; Spielberger, A.; Gspaltl, P. "10th International Symposium on Organosilicon Chemistry, 1993, Poznań, Poland"; Abstracts, p. 265.
- (88) West, R. *J. Organomet. Chem.* **1986**, *300*, 327; Worsfold, D. *J. ACS Symp. Ser.* **1988**, *360*, 101-111; Jones, R. G.; Benfield, R. E.; Cragg, R. H.; Swain, A. C.; Webb, S. *J. Macromolecules* **1993**, *26*, 4878.
- (89) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139.
- (90) Carberry, E.; West, R. *J. Organomet. Chem.* **1966**, *6*, 582.
- (91) Kumada, M.; Sakamoto, S.; Ishikawa, M. *J. Organomet. Chem.* **1969**, *17*, 231.
- (92) Hatanaka, Y.; Hiyama, T. "40th Symposium on Organometallic Chemistry, 1993, Sapporo, Japan"; Abstracts, p. 136.
- (93) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046.
- (94) Suzuki, M.; Kotani, J.; Gyobu, S.; Kaneko, T.; Saegusa, J. *Macromolecules* **1994**, *27*, 2360.
- (95) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641; Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494; *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1993**, *34*, 218.
- (96) Dervan, P. B.; Shippey, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 1265.
- (97) Reetz, M. T.; Plachky, M. *Synthesis* **1976**, 199.
- (98a) Zhivotovskii, D. B.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326; Zhivotovskii, D. B.; Zharov, I.; Apeloig, Y. "10th International Symposium on Organosilicon Chemistry, 1993, Poznań, Poland"; Abstracts, p. 295.
- (98b) Oehme, H.; Wustrack, R.; Heine, A.; Sheldrick, G. M.; Stalke, D. *J. Organomet. Chem.* **1993**, *452*, 33.
- (99a) Sharma, S.; Oehlschlager, A. C. *Tetrahedron* **1989**, *45*, 557.
- (99b) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5383.
- (99c) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1991**, *56*, 770.
- (99d) Singer, R. D.; Oehlschlager, A. C. *J. Org. Chem.* **1991**, *56*, 3510.
- (100a) Colvin, E. W. "Silicon Reagents in Organic Synthesis"; Academic Press: San Diego, 1988; pp. 27, 60.
- (100b) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1805.
- (100c) Fleming, I. *Pure Appl. Chem.* **1988**, *60*, 71.
- (100d) Fleming, I. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 3363, and references cited therein.
- (100e) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.
- (100f) Smith, J. G.; Drozda, S. E.; Petraglia, S. P.; Quinn, N. R.; Rice, E. M.; Taylor, B. S.; Viswanathan, M. *J. Org. Chem.* **1984**, *49*, 4112.
- (101) Lipshutz, B. H.; Reuter, D. C.; Ellsworth, E. L. *J. Org. Chem.* **1989**, *54*, 4975.
- (102) Hiyama, T.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1985**, *105*, 4491.

- (103) Hibino, J.-I.; Nakatsukasa, S.; Fugami, K.; Matsubara, S.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 6416.
- (104) Eades, R. A.; Dixon, D. A. *J. Chem. Phys.* **1980**, *72*, 3309; Sheldon, J. C.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 6794; Damewood, Jr., J. R.; Hadad, C. M. *J. Phys. Chem.* **1988**, *92*, 33; Ortiz, J. V. *ibid.* **1987**, *109*, 5072.
- (105) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998; *Tetrahedron* **1981**, *37*, 1105.
- (106) Magnusson, E. *Tetrahedron* **1985**, *41*, 2945.
- (107a) Hopkinson, A. C.; Lien, M. H. *J. Mol. Struct.* **1983**, *104*, 303.
- (107b) Hopkinson, A. C.; Lien, M. H. *J. Organomet. Chem.* **1981**, *206*, 287.
- (108a) von Schleyer, P. R.; Clark, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1371.
- (108b) von Schleyer, P. R.; Reed, A. E. *J. Am. Chem. Soc.* **1988**, *110*, 4453.
- (108c) Rajca, A.; Wang, P.; Streitwieser, A.; von Schleyer, P. R. *Inorg. Chem.* **1989**, *28*, 3064.
- (108d) Luke, B. T.; Pople, J. A.; Jespersen, M. B. K.; Apeloig, Y.; Chandrasekhar, J.; von Schleyer, P. R. *J. Am. Chem. Soc.* **1986**, *108*, 260.
- (109) Clark, T.; von Schleyer, P. R. *J. Organomet. Chem.* **1980**, *191*, 347.
- (110) Reiter, B.; Hassler, K. *J. Organomet. Chem.* **1994**, *467*, 21.
- (111) Gilman, H.; Shiina, K.; Aoki, D.; Gaj, B. J.; Wittenberg, D.; Brennan, T. *J. Organomet. Chem.* **1968**, *13*, 323.
- (112) Ilsley, W. H.; Sadurski, E. A.; Schaaf, T. F.; Albright, M. J.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1980**, *190*, 257.
- (113) Steward, O. W.; Heider, G. L.; Johnson, J. S. *J. Organomet. Chem.* **1979**, *168*, 33.
- (114) Hengge, E.; Mitter, F. K. *Monatsh. Chem.* **1986**, *117*, 721.

# **Not for Synthesis Only: The Reactions of Organic Halides with Metal Surfaces**

JOHN S. THAYER

*Department of Chemistry  
University of Cincinnati  
Cincinnati, Ohio*

I. Some Basic Considerations . . . . .	59
A. Introduction . . . . .	59
B. Selected Physical Properties . . . . .	60
C. Selected Chemical Aspects . . . . .	61
II. Halide Adsorption on Metal Surfaces . . . . .	63
A. Introduction . . . . .	63
B. Carbon-Halogen Bond Scission. . . . .	63
C. Fragmentation of Adsorbed Alkyl Groups . . . . .	64
III. Mechanistic Investigations of Applied Reactions. . . . .	65
A. Introduction . . . . .	65
B. Grignard Reaction Mechanism Studies . . . . .	66
C. The Direct Process Reaction. . . . .	67
D. Other Applied Syntheses . . . . .	68
IV. Nonsynthetic Applications . . . . .	69
A. Introduction . . . . .	69
B. Nonaqueous Systems . . . . .	70
C. Aqueous Systems . . . . .	70
V. Conclusions . . . . .	74
References . . . . .	75

## **I**

### **SOME BASIC CONSIDERATIONS**

#### **A. Introduction**

The reaction of alkyl halides with metals has played a crucial role in the development of organometallic chemistry. Sir Edward Frankland's synthesis of dialkylzinc compounds (1,2) and subsequent use of those compounds as reagents established the foundations of organometal synthesis (3). Grignard's investigations into the formation of ethereal solutions of organomagnesium compounds from alkyl halides and magnesium metal so greatly expanded and diversified synthetic uses for alkylmetals (3-5) that the Grignard reagent has probably become the single most widely used reagent in organic chemistry. Industrial development of the Direct

Process Reaction and its application to the preparation of silicone precursors (6-9), plus a corresponding industrial preparative method for tetraalkyllead compounds (10), spurred further investigations into the use of direct reactions between solid metals and liquid alkyl halides to synthesize alkylmetal derivatives, generating an extensive literature on this subject (3,4,11).

Studies on mechanistic aspects of such reactions have been relatively sparse. This article will explore recent work on both mechanistic and practical aspects of the direct reaction between metals and halides.

### B. Selected Physical Properties

One characteristic property that all organic halides possess is a carbon-halogen bond dipole moment. The halogen atom is always the negative pole of this bond, and determines the extent of the polarity, with some modification by the organic group. Values for these bond dipole moments (12) and the molecular dipole moments for the two simplest alkyl halide series (13,14) appear in Table I. Interestingly, the carbon-halogen polarity *increases* from fluorine to chlorine! Organic fluorides have been little studied in respect to their reactivity towards metals and are not considered in this article.

Another characteristic property of organic halides is the bond dissociation energy. Table II lists bond energy values for carbon-halogen linkages

TABLE I  
SOME SELECTED DIPOLE MOMENTS

Compound	Dipole moment ( <i>D</i> )	Reference
Bond dipole moments		
C-F	1.41	(12)
C-Cl	1.46	(12)
C-Br	1.38	(12)
C-I	1.19	(12)
Molecular dipole moments		
CH <sub>3</sub> F	1.81	(13)
CH <sub>3</sub> Cl	1.86	(13)
CH <sub>3</sub> Br	1.78	(13)
CH <sub>3</sub> I	1.59	(13)
C <sub>2</sub> H <sub>5</sub> F	1.96	(14)
C <sub>2</sub> H <sub>5</sub> Cl	2.00-2.05	(14)
C <sub>2</sub> H <sub>5</sub> Br	1.99-2.02	(14)
C <sub>2</sub> H <sub>5</sub> I	1.87-1.95	(14)

and for bonds between carbon and elements of the neighboring groups (15-19). It is worth noting that the carbon-halogen bond energies tend to be slightly higher than those for the neighboring elements of the same period. However, their markedly higher bond polarity renders them much more reactive. Organic halides are used as starting materials in many organic syntheses.

For metals, the nature of the active metal surface determines its reactivity, as do both surface cleanness and metal particle size (4,9-11). Finely divided metals, with their correspondingly larger surface areas, show markedly greater reactivity towards alkyl halides than do corresponding bulk metals (20). Sono-chemical treatment of metal surfaces removes impurities and renders such surfaces correspondingly more reactive (21). Various other factors about metal surfaces that affect their adsorption of organic molecules are discussed in a book by Albert and Yates (22).

### C. Selected Chemical Aspects

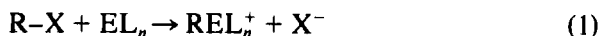
Perhaps the best-known reaction of alkyl halides is oxidative addition to another atom. For elements (usually, nonmetals or metalloids) having

TABLE II  
SELECTED ELEMENT-CARBON BOND ENERGIES

Bond	Energy (kJ/mol)	Reference
P-C	264	(15)
	276	(16)
	260	(17)
As-C	229	(16)
Sb-C	214	(16)
S-C	291	(18)
	270	(17)
Se-C	250	(18)
Te-C	(220)	<sup>a</sup>
Cl-C	327	(15)
	335	(17)
	347	(19)
Br-C	285	(15)
	205	(17)
	294	(19)
I-C	213	(15)
	226	(17)
	243	(19)

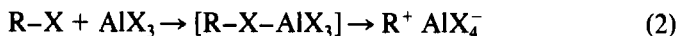
<sup>a</sup> Estimated by author.

a nonbonding pair of electrons in the valence shell, the reaction yields an onium cation:



This reaction also occurs for those derivatives of representative and transition metals in which the metal atom can be oxidized, and was recently used to prepare the first methylnickel(IV) compounds (23).

The halogen atoms in organic halides contain electron pairs in their valence shells and behave as Lewis bases. In this respect, organic halides may be considered as analogous to alkyl derivatives of the corresponding elements of the two preceding periodic groups. However, although hundreds of complexes between triorganophosphines, -arsines, or -stibines and transition metals have been reported, as have a respectable number of corresponding complexes for diorganosulfides, -selenides, and -tellurides, only a very few analogous complexes between alkyl halides and transition metals have been isolated as well as characterized (24,25). One such complex is shown in Fig. 1. This complex contains an iridium atom in the oxidation state of +3, which state is very resistant to further oxidation; such resistance may account for the complex's reported stability (24). Metal-alkyl halide complexes may form as intermediates in Friedel-Crafts reactions (26,27):



The lone pairs on the halogen atoms occur in *p*-orbitals, and readily interact with acceptor orbitals on metals. By the aforementioned analogy to Groups VA and VIA elements, one might expect to encounter electron back-donation from the metal onto the halogen atom (24,25). In methyl iodide (1), the LUMO is a  $\sigma^*$  orbital localized primarily on iodine and is

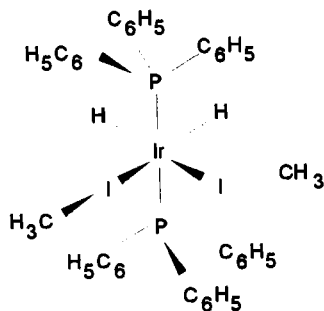


FIG. 1. Geometric structure of  $[IrH_2(ICH_3)_2(P\{C_6H_5\}_3)_2]^+$  cation (24).

a more likely candidate for electron acceptance than the iodine *d*-orbitals (24). Comparative studies indicated that halocarbon binding was enhanced by the electrophilic character of the metal atom, suggesting that back-donation was a minor contributor. Any back-bonding, of course, weakens the carbon-halogen linkage and favors dissociation (25).

## II

### HALIDE ADSORPTION ON METAL SURFACES

#### A. Introduction

Numerous workers have investigated adsorption of alkyl halides onto metal surfaces (28), primarily in order to investigate the ease of carbon-hydrogen bond cleavage. Such studies are usually carried out under conditions of low temperature (<150 K) and high vacuum, using single crystals as substrates (28). Adsorption is molecular, and initial attachment occurs through the halogen atom (28) (Fig. 2). An adsorbed halide might simply be desorbed (released unchanged) or undergo dissociation of the carbon-halogen bond. The tendency to dissociate varies in the following order (28):  $I \gg Br > Cl$ . As a result, alkyl iodides have been used in the majority of reported studies. While in principle any metal might be used as substrate, elements of Groups 10 and 11 (Ni, Pd, Pt, Cu, Ag, Au) have been the metals most frequently investigated, possibly because of their importance in catalysis.

#### B. Carbon-Halogen Bond Scission

When methyl halide monolayers were generated on a Ni(100) surface at 100 K,  $CH_3Cl$  (**2**) desorbed unchanged, while  $CH_3Br$  (**3**) was partly

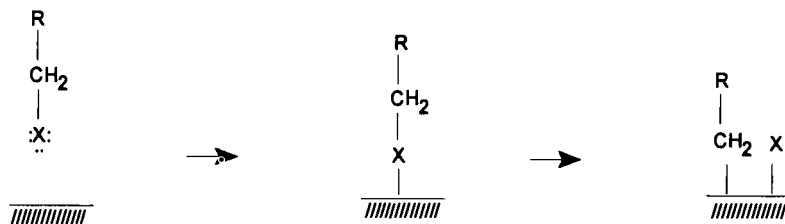


FIG. 2. Bonding of alkyl halides to metal surfaces.



dissociated, and (1) was completely dissociated (29). Molecule (2) decomposed only on Fe or W but not on Ag, Cu, Pt, Pd or Au, while (3) dissociated on Ni (but not on Ag or Pt) and (1) dissociated on all metals tested (28). Carbon-halogen bonds can be broken by thermolysis or photolysis; use of the latter technique has been reviewed (30). A thermal activation energy of approximately 14 kJ/mol for the C-I bond on Ni(100) surfaces has been reported (31). When (1) adsorbed onto a Pd(111) surface, cleavage of the carbon-iodine linkage occurred between 175 and 200 K; on a corresponding Pd(100) surface, scission occurred at 95 K (32). Methyl groups desorbed as methane; no C<sub>2</sub> products formed (32). Pretreatment of the surface with carbon monoxide enhanced the thermal stability of adsorbed methyl groups (32). Photodissociation studies of (3) adsorbed upon a Cu(111) surface (33) or a Cu(111) pretreated with bromine (34) gave results compatible with a mechanism involving photoexcitation of an electron from the metal *d*-band into the carbon-bromine  $\sigma^*$ -orbital. Comparative photochemical studies on Ag(111) surfaces showed that initial photolysis rates for the methyl halides increased going from Cl to I (35-37). Adsorbed halogen atoms remain strongly attached to the metal surface and require much higher temperatures for desorption.

### C. Fragmentation of Adsorbed Alkyl Groups

When the carbon-halogen bond undergoes scission, the resulting alkyl radical adsorbs onto the metal surface (28). Both (3) (33,38) and (1) (39-42) generated surface-bound methyl groups. Ethyl chloride (4) (35) and ethyl iodide (5) (43, 44) formed adsorbed ethyl groups, while both 1- and 2-propyl moieties formed on Ni(100) surfaces from the corresponding propyl iodides (45). At low surface coverage, (5) on Pt(111) formed ethyl groups that were flat against the surface; increasing coverage converted them to an upright position (44). When diiodomethane was adsorbed onto the Al(111) surface at 108 K, both iodine atoms were removed; no evidence for adsorbed ICH<sub>2</sub> groups was reported (46).

Adsorbed alkyl groups usually undergo elimination of an  $\alpha$ -hydrogen to give adsorbed hydrogen and methylane (*cf.* Fig. 3a). Ethyl and longer alkyl groups can also undergo elimination of a  $\beta$ -hydrogen atom to form an alkenyl group (Fig. 3b). Comparative studies indicate that beta-hydrogen elimination occurs at least 10<sup>6</sup> times faster than alpha-hydrogen elimination (47). Desorption usually yielded a mixture of hydrocarbons whose composition varied with temperature.

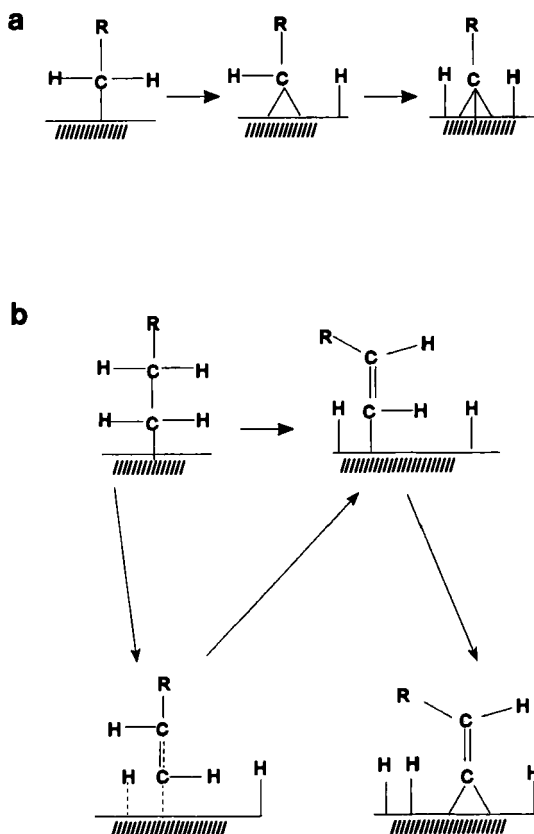


FIG. 3. Hydrogen elimination from alkyl groups adsorbed on metal surfaces: (a)  $\alpha$ -hydrogen; (b)  $\beta$ -hydrogen.

### III

## MECHANISTIC INVESTIGATIONS OF APPLIED REACTIONS

### A. Introduction

Detailed investigations into the mechanism of reaction between alkyl halides and metals have concentrated primarily on systems of great practical interest: the Grignard reaction, the Direct Process Reaction, and a few others. Whereas research reported in the preceding section involved solely pure gaseous halides and pure metals as single crystals, mechanistic investigations have involved a much wider variety of substrates and reaction conditions. When a solvent is involved, solvation of the metal product

provides considerable driving force for the reaction. If the metal substrate is not uniform in composition (i.e., it is an alloy or intermetallic species), electron distribution will also be nonuniform, creating a charge polarity. This polarity will affect interaction with the polar carbon-halogen bond, as shown in Fig. 4; the alkyl group bonds to the atom with the greater electron density. If one metal of a two-metal alloy is an alkali metal, the polarity becomes large enough to make the system quasi-ionic, making the reaction proceed more rapidly and more completely. Interest in semiconductors involving such materials as gallium antimonide and cadmium telluride has also led to studies on the interaction of these materials with alkyl halides.

### B. Grignard Reaction Mechanism Studies

In their early monograph on the Grignard reaction, Kharasch and Reinmuth noted the effects that varying the form of magnesium metal would have on reagent preparation [(4), pp. 6-15]; they also noted that the addition of copper to magnesium lowered the yield of reagent. In a detailed mechanistic study, Rogers *et al.* reported that reaction rates for ethereal organic halides reacting with magnesium depended both on the concentration of halide and on the magnesium surface area (48). They also found that, for alkyl iodides and most alkyl bromides, the rate of reaction was limited by transport to the magnesium surface; this was not true for the chlorides (48). Initiation of the magnesium-halide reaction proceeded through formation of corrosion pits, which would expand and overlap, so that much of the reaction occurred on a shiny surface (49). While reaction rates were not much affected by metal lattice plane or grain boundaries, initiation of reaction occurred more readily at strained dislocations (49). Reactivity increased when small quantities of lithium were alloyed with magnesium and decreased in the presence of more electronegative metals (49). Investigations using EPR spectroscopy indicated that the carbon-halogen bond energy influenced the mechanism of Mg-C bond formation and that radicals and/or ion-radicals were the most likely intermediates (50).

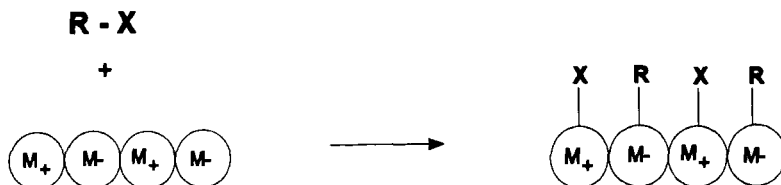


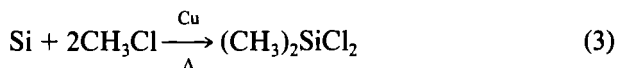
FIG. 4. Effect of metal polarity (M<sub>+</sub> is the more electropositive metal).

High-vacuum studies on the adsorption of methyl bromide on Mg(0001) surfaces at 123 K indicated that reaction occurred readily but that no stable magnesium–carbon bonds formed (51); the methyl group desorbed as a hydrocarbon mixture, with ethane as the primary component. An activation energy of 25–33 kJ/mol was estimated (51). The presence of coadsorbed dimethyl ether did not affect the reaction. When magnesium metal and methyl halides were codeposited in an argon matrix, they were found by infrared spectroscopy to give cleavage of the carbon–halogen bond, but nothing more could be said about the nature of the product (52). Similar matrix isolation studies using methyl bromide and clusters of magnesium atoms gave evidence for the formation of  $\text{CH}_3(\text{Mg})_x\text{Br}$  species (53).

There has been some controversy over the nature of intermediates in the Grignard reaction (54–56). Available evidence indicates that organic radicals form through cleavage of the carbon–halogen linkage; everyone agrees on this. Controversy centers on the question of whether the alkyl radical remains adsorbed on the metal surface (“A model”) or whether it diffuses into solution (“D model”). Evidence appears to be more consistent with the “D model” (56), but the question cannot be considered as settled.

### C. The Direct Process Reaction

As previously mentioned, the Direct Process Reaction involves the reaction of (2) with silicon at elevated temperatures to form methylchlorosilanes (6–9):



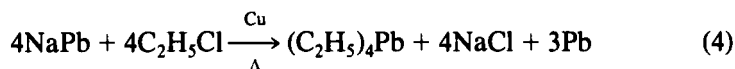
This equation is a major oversimplification; a mixture of many silicon-containing products actually forms. Their proportions may be controlled by adjusting reaction conditions. In fact, research has concentrated on determining those conditions that favor formation of one specific product. Pure silicon is not used; instead, copper must be added as a catalyst. The addition of trace metals such as zinc, aluminum, and/or tin tends to increase reaction rates and to favor the formation of dimethyldichlorosilane over other products (57). Two recent patents pertaining to the preparation of the silicon–copper catalyst have been issued (58,59).

A critical review of proposed mechanisms for the direct process has recently appeared (60). The authors proposed that an atom of silicon bonds to copper and behaves as a silylene (i.e., has electron density

exceeding that of an ordinary silicon atom). This silylene subsequently reacts with methyl chloride to undergo oxidative addition, forming adsorbed methylsilicon(II) chloride (Fig. 5a), which then reacts further to yield various products. Other reported reactions of silicon are also consistent with this mechanism (61). By contrast (but consistent with other single-crystal work previously cited), adsorption of (1) onto a Si(100) surface resulted in the finding of the methyl group and the iodine atom to separate silicon atoms (62) [Fig. 5b]. A study of Si(100) crystals and various forms of copper catalysts indicated that  $\text{Cu}_3\text{Si}$  (6) formed in most cases, but that the reactivity and selectivity for dimethyldichlorosilane varied quite markedly (63); the most reactive surfaces had a randomly oriented (6) phase.

#### D. Other Applied Syntheses

The reaction of (4) with a sodium-lead alloy has long been used for the industrial preparation of tetraethyllead (7) (10,64). Traditionally the reaction has been written:



The sodium-lead alloy has to be specifically prepared (65), and quite a variety of reaction conditions have been reported (10). The surface needs to be oxygen free. Partial replacement of sodium by potassium enhances yields, as does treatment with iodine. The system's temperature and pressure of (4) also are crucial factors in determining reaction rate. The following mechanism was proposed (10):

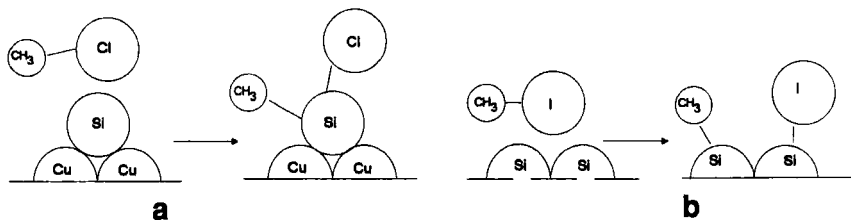
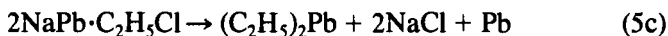
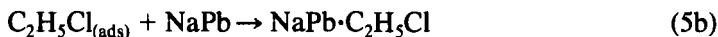
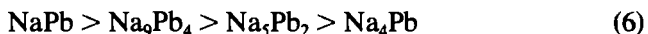


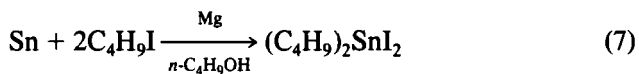
FIG. 5. Attachment of methyl halides to silicon atoms: (a) copper silicide; (b) silicon single crystal.

The species "NaPb·C<sub>2</sub>H<sub>5</sub>Cl" is probably "Na·C<sub>2</sub>H<sub>5</sub>PbCl." Under the conditions of the reaction, adsorbed diethylplumbylene reacts to form (7) or triethyllead species. Reaction occurs slowly or not at all if the sodium content of the alloy becomes too high:

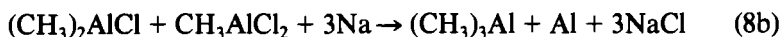


Halides containing longer-chain alkyl groups reacted more slowly. Unalloyed lead metal reacted with alkyl halides, especially if it was oxide free and finely divided (10). Binary alloys of lead with other active metals have also been tried as substrates, with varying success (10).

The use of a sodium-tin alloy for the preparation of tetramethyltin preceded use of the corresponding sodium-lead alloy (64,66), but was subsequently displaced by other methods. Currently, the Direct Reaction is used to prepare dialkyltin dihalides, and generally requires an oxygen-containing solvent plus another metal as "accelerator" (66):



The Direct Reaction between aluminum and (2) is used to prepare trimethylaluminum (67):



The growing use of trialkylgallium and -indium compounds in the synthesis of semiconductors has led to the issuance of patented methods for their preparation from metal-magnesium alloys and alkyl halides (68-71). Other such preparations are likely to appear as the need for alkylmetal compounds increases.

## IV

### NONSYNTHETIC APPLICATIONS

#### A. Introduction

Investigations into nonsynthetic aspects of the Direct Reaction have usually focused on their possible uses to extract metals from solids. The substrate may be a pure metal, a metal alloy, or a compound between a metal and a semimetal. In these applications, the yield may or may not be important. It is not even necessary that the metal-carbon bond be sufficiently stable to isolate the alkylmetals formed; even if the initially

formed species exist for only a second or less, that may still be sufficient for the purposes of the process. The crucial aspect is that the metal atom reacts with the alkyl halide, and in so reacting becomes detached from the solid substrate. Metal removal through alkylmetal formation may be deliberate (as in etching or extraction) or unintended (as in corrosion). Such processes have been investigated under both nonaqueous and aqueous conditions.

### B. *Nonaqueous Systems*

Growing interest in the use of III/V compounds, e.g., GaAs (**8**), as semiconducting materials has encouraged extensive investigations into processes for etching these materials. Organic halides have been used, primarily as a halogen source, in photochemical etching of indium phosphide (**9**) (72,73) and (**8**) (74,75). Rates of etching were measured for (**8**) and AlGaAs, using (**1**) [ $\text{CH}_3\text{I}$ ] vapor in a carrier gas at various temperatures (76). Similar studies using  $\text{CF}_3\text{Cl}$  on these materials showed that etching rates decreased as the mole fraction of Al increased (74). Treatment of the (111) faces of (**9**) with unsubstituted benzyl bromides gave substitution on exposed phosphorus atoms of the P-rich (111)B face, but not on indium atoms of the In-rich (111)A face (77). To date, all reports on reactions between III/V materials and alkyl halides indicate that only the Group V atom actually forms a bond to a carbon atom of the alkyl moiety.

Corrosion studies have been rare. (**8**), copper, or iron were corroded by carbon tetrachloride when exposed to Co-60 radiation (78). Alkyl halides enhanced the corrosive effect of benzoic acid on iron (79). (**1**) was found to promote stress-corrosion cracking in zirconium alloys used in nuclear reactors (80).

### C. *Aqueous Systems*

#### 1. *General Considerations*

Addition of water to a metal–organic halide system alters the nature of the reaction medium considerably, and can cause various side reactions:

- a. *Reaction with metal*—Water can react with many metals, especially if these are present as finely divided, highly reactive powders. If the water is acidic, such reactivity increases. Dissolution of metals in an acidic medium proceeds considerably faster than the corresponding dissolution by alkyl halides.

- b. *Hydrolysis of the alkyl halide*—This side reaction is especially important for secondary and tertiary alkyl halides, which react with water more rapidly than their primary counterparts. In addition to destroying the halide reactant, hydrolysis generates strongly acidic hydrogen halides, resulting in the complications noted in part (a).
- c. *Reaction with the metal product*—Water can react with the very polar metal-halide and metal-alkyl bonds. Both bonds are broken, generating metal-hydroxide linkages. For many metals, most notably iron, these hydroxy products show very low solubility in water, even acidic water, and will coat the surface of the metal, hampering and complicating further reaction.

The solubility of most alkyl halides in water is very low, unless some solubilizing group happens to be present (e.g.,  $-\text{OH}$ ,  $-\text{CO}_2\text{H}$ ). Hence, most reaction systems have involved three separate phases (water, halide, metal substrate), with all the accompanying complications.

Interest concerning the Direct Reaction in aqueous systems has arisen from association with two burgeoning areas of research: environmental formation of alkyl (mostly methyl) derivatives of metals, and corrosion of metal surfaces exposed to water. These will be considered separately.

### 2. *Environmental Methylmetal Formation*

Interest and concern about environmental occurrence of methylmetal derivatives grew out of the extensive poisoning by methylmercuric derivatives in Minamata Bay (Japan) and elsewhere (81,82). Methylation can occur either through biological intermediation ("biological methylation") or by abiotic methyl exchange. The great majority of substrates in both types of methylation are metal ions or metal compounds. However, metallic tin and lead are known to react with (1) to form methylmetal compounds (83,84), and other metals or metalloids probably behave similarly. Methyl halides, along with other organohalogen compounds, form through biogenic processes and occur in nature in substantial quantities (85-87). These compounds may well play a role in the environmental cycles of metals (88).

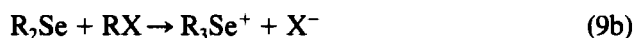
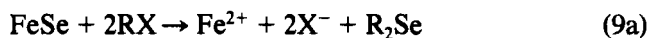
### 3. *Metal Leaching and Corrosion*

In 1977, Mor and Beccaria investigated the roles of alkyl bromides and iodides on the corrosion of copper in seawater (89). They found that alkyl bromides enhanced the corrosion of copper, whereas alkyl iodides inhibited it, perhaps by lowering the pH of the system (89). A wide variety



of binary metal species released metals into aqueous solution when treated with alkyl halides (90–92). Many of these are shown in Table III. Treatment of (8) with aqueous alkyl halides gave dissolution of arsenic as methylarsonic or cacodylic acids, but no dissolution of gallium (93).

All reported work on binary systems containing a metal and a second element indicate that the more electronegative element, which presumably has a higher electron density, forms a bond to a carbon atom in the alkyl group, while the halogen atom bonds to the other atom or is reduced to a halide ion. If the second element is a chalcogen, volatile dialkylchalconides and/or water-soluble trialkylchalconium ions form as products:



For arsenic, the water-soluble methylarsonic and cacodylic acids are apparently the major products, and presumably similar products are formed also for phosphorus and antimony (93).

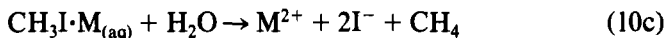
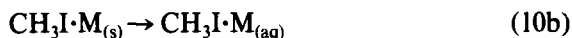
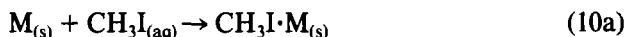
Various metals, when treated with aqueous (1) or other alkyl iodides under flow conditions, showed marked dissolution into water (91,94–96). Dissolution also occurred under static conditions (92,95,97). Initially, these studies used metals more active than hydrogen (Fe, Cr, Ni, Zn, Sn, Pb, Mn); however, Cu was also found to undergo similar dissolution. Preliminary investigations indicated that metallic silver readily formed silver bromide in the presence of alkyl bromides and that palladium dis-

TABLE III  
METAL SPECIES REACTED WITH ALKYL HALIDES<sup>a</sup>

Compounds		Ores
AsS <sub>2</sub>	Cu <sub>3</sub> Si	Arsenopyrite (FeAsS)
FeS	FeSi	Chalcopyrite (CuFeS <sub>2</sub> )
	GaAs	Enargite (Cu <sub>3</sub> AsS <sub>4</sub> )
HgS	GaSb	Galena (PbS)
MnS	InAs	Niccolite (NiAs)
MoS <sub>2</sub>	InSb	Pyrrite (FeS <sub>2</sub> )
PbS	Ni <sub>2</sub> P	Pyrrhotite (FeS)
SnS	NiAs	Stibnite (Sb <sub>2</sub> S <sub>3</sub> )
FeSe		
FeTe		
PbSe		
PbTe		

<sup>a</sup> Taken from Thayer *et al.* (90).

solved to some extent when treated with certain aqueous alkyl bromides (98). We proposed the following mechanism for reaction between a metal and (1) (90):



When copper or iron strips were placed in water after long exposure to benzyl bromide vapors, they showed much greater dissolution than unexposed strips (Table IV) (97). Replacement of water by deuterium oxide as the reaction medium yielded  $CH_3D$  as the primary gaseous products (97). While this would arise from the hydrolysis of a metal-methyl bond:



there was in this case insufficient evidence to indicate whether the methylmetal species was still present on the substrate surface or had already diffused into solution.

The initial step (eq. 10a) in the proposed mechanism requires adsorption/binding of the alkyl halide to the metal surface—a process already previously discussed. Anything that might enhance this adsorption should affect the rate and extent of reaction. We have found that  $\omega$ -bromo-1-alkenes enhanced copper dissolution from alloys (Table V). Comparative studies on brass foil confirmed these observations and also showed that the dissolution of zinc was affected only slightly (Table VI). The compound

TABLE IV  
METAL-BENZYL BROMIDE VAPOR REACTION<sup>a</sup>

Elapsed time (hours)	Copper		Nickel		Molybdenum	
	Control	Reaction	Control	Reaction	Control	Reaction
2	0.10	1.42	0.11	0.50	1.44	1.74
24	0.40	2.42	0.20	1.13	4.00	6.00
48	0.44	2.44	0.22	1.50	6.00	15.20

<sup>a</sup> Strips of Cu, Mo, or Ni were placed in a sealed dessicator with an open container of benzyl bromide, and exposed to the vapor for eight days. Corresponding "control" strips were kept in a dessicator for the same period. All strips were then withdrawn and placed into 50-mL portions of distilled water. Aliquots were withdrawn to test for dissolved metal levels. All dissolved metal concentrations have units of mg/L. Molybdenum concentrations were determined as molybdate ion.

TABLE V  
DISSOLUTION OF COPPER FROM BRONZE POWDER<sup>a</sup>

Alkyl bromide	[Cu], mg/L
None (control)	0.06
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> Br	0.4
CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> Br	2.4
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	0.2
CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> Br	0.37
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> Br	0.01
CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>4</sub> Br	0.03

<sup>a</sup> 46.97 ± 0.20 mg bronze powder (90% Cu; 10% Sn; particle size 45–53 μm) was treated with 25 mL water and 0.20 mL RBr for five days.

TABLE VI  
UNIT DISSOLUTION RATES OF ZINC AND COPPER FROM BRASS FOIL IN AERATED WATER<sup>a</sup>

Metal	Alkyl halide	Rate (μg/S·m <sup>2</sup> )
Zinc	None	7.00
	CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> Br	7.20
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> Br	11.00
	CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	4.70
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> Br	7.20
Copper	None	1.00
	CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> Br	2.10
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> Br	10.00
	CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	1.40
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> Br	6.80

<sup>a</sup> Data taken from Thayer (94).

7-bromoheptanenitrile gave similar results (95). We attributed this effect to the ability of copper to form a  $\pi$ -complex with the carbon-carbon double bond, thereby favoring binding of the reactant halide to copper and facilitating subsequent reaction (95).

## V

## CONCLUSIONS

Every example of the Direct Reaction, whether used for synthesis or not, involves removal of metal atoms from a solid matrix through formation

of metal-carbon bonds. Most investigations have centered on isolation and/or stabilization of the alkylmetal compounds for subsequent synthetic usage. However, there is a growing number of applications that utilize the oxidizing nature of the Direct Reaction and do not require isolation of the alkylmetal product. Steady expansion of interest in the properties of semiconducting materials suggests that the use of alkyl halides as etching chemicals will likewise expand. The selective alkylation of the phosphorus atoms of (9) (77) raises the possibility that alkyl halides with a fluorescent- or otherwise-labeled alkyl group might be used to mark atoms selectively on a solid surface.

Apart from the Grignard reaction and the industrial preparation of alkyl-leads, solutions of alkyl halides as reactants have received relatively little attention. A 6:1 solution of (1)/acetic acid could be used to reclaim rhodium from used catalyst waste (99). The possibility of using aqueous alkyl halides for leaching has been proposed elsewhere (94). Other binary or ternary mixtures containing alkyl halides may well find important applications not yet suspected.

While the Direct Reaction causes the oxidization of a metal and removes it from a solid, it also results in the destruction of carbon-halogen bonds. Since many anthropogenic organic chlorides or bromides are major pollutants, reaction with metals provides one potential route for their detoxification. At least one patent has been issued for this application (100).

The Direct Reaction has been known for almost 150 years. Over that time its scope and usage have expanded enormously. While research on this reaction has been quite extensive, investigations have tended to focus on certain subareas, with little or no interaction among them. When this changes, understanding of details about a very diversified reaction should expand accordingly, and new combinations of metals and organic halides should suggest themselves for investigation. Thus the Direct Reaction, one of the oldest reactions in Chemistry, remains one of the most multifaceted and dynamic, showing every sign of continuing and developing for another 150 years.

#### REFERENCES

- (1) Frankland, E. *J. Chem. Soc.* **1849**, 2, 263.
- (2) Frankland, E. *J. Chem. Soc.* **1849**, 2, 294.
- (3) Thayer, J. S. *Adv. Organomet. Chem.* **1975**, 13, 1.
- (4) Kharasch, M. S.; Reinmuth, O. "Grignard Reactions of Nonmetallic Substances"; Prentice-Hall: New York, 1954.
- (5) Thayer, J. S. *J. Chem. Educ.* **1969**, 46, 764.
- (6) Rochow, E. G. "An Introduction to the Chemistry of the Silicones"; Wiley: New York, 1946.

- (7) Rochow, E. G. *Adv. Organomet. Chem.* **1970**, *9*, 1.
- (8) Liebhafts, H. A. "Silicones Under the Monogram"; Wiley: New York, 1978.
- (9) Rochow, E. G. "Silicon and Silicones"; Springer-Verlag: Berlin, 1987.
- (10) Shapiro, H.; Frey, F. W. "The Organic Compounds of Lead"; Wiley: New York, 1968; pp. 34-44.
- (11) Rochow, E. G. *J. Chem. Educ.* **1966**, *43*, 58.
- (12) Wagniere, G. H. In "The Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: London, 1973; p. 21.
- (13) Smith, R. P.; Ree, T.; Magee, J. L.; Eyring, H. *J. Am. Chem. Soc.* **1951**, *73*, 3932.
- (14) Smith, R. P.; Mortensen, E. M. *J. Am. Chem. Soc.* **1956**, *78*, 2263.
- (15) Huheey, J. A.; Keiter, E. A.; Keiter, R. L. "Inorganic Chemistry"; 4th ed.; Harper Collins: New York, 1993; p. A-30.
- (16) Elschenbroich, C.; Salzer, A. "Organometallics: A Concise Introduction"; 2nd ed.; VCH Publishers: Weinheim, 1992; p. 11.
- (17) Douglas, B.; McDaniel, D.; Alexander, J. "Concepts and Models of Inorganic Chemistry"; 3d ed.; Wiley: New York, 1994; p. 89.
- (18) Batt, L. In "The Chemistry of Organic Selenium and Tellurium Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1986; Vol. 1, p. 159.
- (19) Chen, E. C. M.; Albyn, K.; Dussack, L.; Wentworth, W. E. *J. Phys. Chem.* **1988**, *93*, 6827.
- (20) Rieke, R. D. *Science* **1989**, *246*, 1260.
- (21) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73.
- (22) Albert, M. R.; Yates, J. T. "The Surface Scientist's Guide to Organometallic Chemistry"; American Chemical Society: Washington, DC, 1987.
- (23) Klein, H.; Bickelhaupt, A.; Jung, T.; Cordier, G. *Organometallics* **1994**, *13*, 2557.
- (24) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241.
- (25) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *J. Organomet. Chem.* **1988**, *341*, 495.
- (26) Olah, G. A. "Friedel-Crafts Chemistry"; Wiley: New York, 1973.
- (27) Roberts, R. M.; Khalaf, A. A. "Friedel-Crafts Alkylation Chemistry"; Dekker: New York, 1984.
- (28) Zaera, F. *Acct. Chem. Res.* **1992**, *25*, 260.
- (29) Zhou, X. L.; Whike, J. M. *Surf. Sci.* **1988**, *194*, 438.
- (30) Zhou, X. L.; Zhu, X. Y.; White, J. M. *Acc. Chem. Res.* **1990**, *23*, 327.
- (31) Tjandra, S.; Zaera, F. *J. Vac. Sci. Technol., A* **1992**, *10*, 404.
- (32) Chen, J. J.; Winograd, N. *Surf. Sci.* **1994**, *314*, 288.
- (33) Lamont, C. L. A.; Conrad, H.; Bradshaw, A. M. *Surf. Sci.* **1993**, *280*, 79.
- (34) Lamont, C. L. A.; Conrad, H.; Bradshaw, A. M. *Surf. Sci.* **1993**, *287*, 169.
- (35) Zhou, X. L.; White, J. M. *Surf. Sci.* **1991**, *241*, 244.
- (36) Zhou, X. L.; White, J. M. *Surf. Sci.* **1991**, *241*, 259.
- (37) Zhou, X. L.; White, J. M. *Surf. Sci.* **1991**, *241*, 270.
- (38) Radhakrishnan, G.; Stenzel, W.; Hemmen, R.; Conrad, H.; Bradshaw, A. M. *J. Chem. Phys.* **1991**, *95*, 3930.
- (39) Solymosi, F.; Revesz, K. *J. Am. Chem. Soc.* **1991**, 9145.
- (40) Chiang, C.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.
- (41) Lin, J.; Bent, B. E. *J. Am. Chem. Soc.* **1992**, *115*, 2849.
- (42) Chen, J. J.; Winograd, N. *Surf. Sci.* **1994**, *314*, 188.
- (43) Jenks, C. J.; Lin, J. L.; Chiang, C. M.; Kang, L.; Leang, P. S.; Wentzlaff, T. H.; Bent, B. E. *Stud. Surf. Sci. Catal.* **1991**, *67*, 301.
- (44) Hofmann, H.; Griffiths, P. R.; Zaera, F. *Surf. Sci.* **1992**, *262*, 141.
- (45) Tjandra, S.; Zaera, F. *Langmuir* **1994**, *10*, 2640.
- (46) Hara, M.; Domen, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1717.

- (47) Jenks, C. J.; Chiang, M.; Bent, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 6308.
- (48) Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217.
- (49) Hill, C. L.; Vander Sande, J. B.; Whitesides, G. M. *J. Org. Chem.* **1980**, *45*, 1020.
- (50) Sergeev, G. B.; Zagorsky, V. V.; Badaev, F. Z. *J. Organomet. Chem.* **1983**, *243*, 123.
- (51) Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 2881.
- (52) Ault, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 3480.
- (53) Imizu, Y.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 3602.
- (54) Walborsky, H. M. *Acct. Chem. Res.* **1990**, *23*, 286.
- (55) Garst, J. F. *Acct. Chem. Res.* **1991**, *24*, 95.
- (56) Walling, C. *Acct. Chem. Res.* **1991**, *24*, 255.
- (57) Gasper-Galvin, L. D.; Sevenich, D. M.; Friedrich, H. B.; Rethwisch, D. G. *J. Catal.* **1991**, *128*, 468.
- (58) Mui, J. Y. P. *Chem. Abstr.* **1994**, *129*, 30932u.
- (59) Streckl, W.; Straussberger, H.; Pachaly, B. *Chem. Abstr.* **1994**, *120*, 5469r.
- (60) Lewis, K. M.; McLeod, D.; Kanner, B.; Falconer, J. L.; Frank, T. In "Studies in Organic Chemistry. 49. Catalyzed Direct Reactions of Silicon"; Lewis, K. M.; Rethwisch, D. S., Eds.; Elsevier: Amsterdam, 1993, pp. 333–440.
- (61) Ono, Y.; Okano, M.; Watanabe, N.; Suzuki, E. In "Silicon for the Chemical Industry II"; Oye, H. A.; Rong, H. M.; Nygaard, L.; Schuessler, G.; Tuset, J. K., Eds.; Tapir Forlag: Trondheim, Norway, 1994; pp. 185–196.
- (62) Gutleben, H.; Lucas, S. R.; Cheng, C. C.; Choyke, W. J.; Yates, J. T. *Surf. Sci.* **1991**, *257*, 146.
- (63) Floquet, N.; Yilmaz, S.; Falconer, J. L. *J. Catal.* **1994**, *148*, 348.
- (64) Nickerson, S. P. *J. Chem. Educ.* **1954**, *31*, 560.
- (65) Shapiro, H. *Adv. Chem. Ser.* **1959**, *23*, 290–298.
- (66) Omae, I. *J. Org. Chem., Libr.* **1989**, *21*, 35–48.
- (67) Eisch, J. J. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 1, p. 560.
- (68) Imori, T.; Kondo, K.; Ninomya, T.; Nakamura, K. *Chem. Abstr.* **1991**, *115*, 159431f.
- (69) Imori, T.; Kondo, K.; Ninomya, T.; Nakamura, K. *Chem. Abstr.* **1991**, *115*, 159432g.
- (70) Ninomya, T.; Kondo, K.; Imori, T.; Nakamura, K. *Chem. Abstr.* **1991**, *115*, 280275m.
- (71) Smit, C. J.; Van Hunnik, E. W. J.; Van Eijden, G. J. M. *Chem. Abstr.* **1993**, *119*, 8125m.
- (72) Haigh, J.; Aylett, M. R. *Chem. Abstr.* **1987**, *106*, 128994b.
- (73) Durose, K.; Summersgill, J. P. L.; Aylett, M. R.; Haigh, J. *Chem. Abstr.* **1990**, *112*, 26318r.
- (74) Seabaugh, A. *J. Vac. Sci. Technol., B* **1988**, *6*, 77.
- (75) Buhaenko, D. S.; Francis, S. M.; Goulding, P. A.; Pemble, M. E. *Stud. Surf. Sci. Catal.* **1988**, *48*, 229.
- (76) Krueger, C. W.; Wang, C. A.; Flytzani-Stephanopoulos, M. *Appl. Phys. Lett.* **1992**, *60*, 1459.
- (77) Spool, A. M.; Daube, K. A.; Mallouk, T. E.; Belmont, J. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3155.
- (78) Proesch, U.; Sander, R. *Isotopenpraxis* **1990**, *26*, 469; *Chem. Abstr.* **1991**, *114*, 52708d.
- (79) Yamamoto, T.; Imaizumi, K.; Kurata, Y. *Inorg. Chim. Acta* **1984**, *85*, 175.
- (80) Cox, B.; Haddad, R. *J. Nucl. Mater.* **1986**, *137*, 115.
- (81) Sigel, H.; Sigel, A. (Eds.). "Metal Ions in Biological Systems"; Dekker: New York, 1993; Vol. 29.
- (82) Thayer, J. S. "Environmental Chemistry of the Hydrido and Organo Derivatives of the Heavy Elements"; VCH Publishers: New York, 1995.
- (83) Anagnostopoulos, A.; Hadjispyrou, S. *Toxicol. Environ. Chem.* **1993**, *39*, 207.

- (84) Craig, P. J.; Rapsomanikis, S. *Environ. Sci. Technol.* **1985**, *19*, 726.
- (85) Harper, D. B. *Met. Ions Biol. Syst.* **1993**, *29*, 345.
- (86) Harper, D. B. *Biochem. Soc. Trans.* **1994**, *22*, 1007.
- (87) Gribble, G. W. *J. Chem. Educ.* **1994**, *71*, 907.
- (88) Brinckman, F. E.; Olson, G. J., Thayer, J. S. In "Marine and Estuarine Geochemistry"; Sigleo, A. C.; Hattori, A., Eds.; Lewis: Chelsea, MI, 1985; pp. 227-228.
- (89) Mor, E. D.; Beccaria, A. M. *Br. Corros. J.* **1977**, *12*, 243.
- (90) Thayer, J. S.; Olson, G. J.; Brinckman, F. E. *Environ. Sci. Technol.* **1984**, *18*, 726.
- (91) Thayer, J. S.; Olson, G. J.; Brinckman, F. E. *Appl. Organomet. Chem.* **1987**, *1*, 73.
- (92) Thayer, J. S.; Brinckman, F. E. *Abstr. 4th Chem. Congr. North Am.* **1991**, Inor. 80.
- (93) Craig, P. J.; Laurie, S. H.; McDonagh, R. *Appl. Organomet. Chem.* **1994**, *8*, 183.
- (94) Thayer, J. S. *ChemTech.* **1990**, *20*, 188.
- (95) Thayer, J. S. *Appl. Organomet. Chem.* **1993**, *7*, 525.
- (96) Thayer, J. S.; Brinckman, F. E. *Appl. Organomet. Chem.* (submitted for publication).
- (97) Thayer, J. S. *Abstr. 206th Natl. Am. Chem. Soc. Meet.*, **1993**, Inor. 428.
- (98) Thayer, J. S. Unpublished observations.
- (99) Gulliver, D. J. *Chem. Abstr.* **1989**, *111*, 43152d.
- (100) Mandl, J. *Chem. Abstr.* **1990**, *112*, 11530e.

# ***The Bonding of Metal–Alkynyl Complexes***

JOSEPH MANNA, KEVIN D. JOHN, and  
MICHAEL D. HOPKINS

*Department of Chemistry, University of Pittsburgh  
Pittsburgh, Pennsylvania*

I. Introduction . . . . .	79
II. Theoretical and Experimental Background. . . . .	82
A. Molecular-Orbital Calculations and Photoelectron Spectroscopy . . . . .	83
B. Electronic Spectroscopy . . . . .	84
C. Other Physical Studies . . . . .	88
III. X-Ray Crystallographic Studies . . . . .	90
A. Overview . . . . .	90
B. C≡C Bond Distances . . . . .	100
C. M–C Bond Distances . . . . .	105
D. C–R Bond Distances . . . . .	116
E. The Structural <i>Trans</i> Influences of Alkynyl Ligands . . . . .	117
IV. Vibrational Spectroscopic Studies . . . . .	120
A. Overview . . . . .	120
B. C≡C Stretching Frequencies . . . . .	121
C. M–C and C–R Stretching Frequencies . . . . .	138
V. Concluding Remarks . . . . .	139
VI. Appendix: Abbreviations Used in this Review . . . . .	140
References . . . . .	141

## **I**

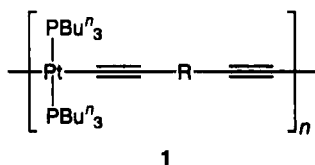
### **INTRODUCTION**

The chemistry of metal–alkynyl compounds is developing at a rapid pace. At the time of the only extensive (though not comprehensive) review of this area, by Nast in 1982 (*1*), the published work on the syntheses, reactions, structures, and properties of complexes, clusters, and polymers containing terminal and bridging alkynyl ligands over the previous 30 years consisted of approximately 200 papers. Since then, nearly 500 papers (200 of which have appeared in this decade) have been published on terminal metal–alkynyl complexes alone. The increasing interest in these compounds has made the need for a new survey of their chemistry an urgent one, although the size of the field, and the diversity of interests within it, has made a comprehensive review an imposing (monograph-scale) task.

The scope of research in metal–alkynyl chemistry is broad; in addition to spanning the general areas of traditional interest to organometallic



chemists, there is an emerging interest in metal-alkynyl complexes regarding their potential materials-science applications. Special attention has been devoted to several subtopics within the field. The  $\text{C}\equiv\text{C}$  bonds of alkynyl ligands, like those of organic alkynes, constitute a natural focal point for reactivity studies, and have been shown to participate in a rich set of chemical transformations. Among the ligand-localized reactions of metal-alkynyl complexes, those that lead to the formation of clusters in which the alkynyl ligand bridges multiple metal centers (2), and in which the alkynyl ligand is transformed into vinylidene or other ligands (3), have been extensively studied. The linear geometry of the  $\text{—C}\equiv\text{C—}$  unit and its potential to act as a “molecular wire” that might enable electronic communication between its appended substituents has made the synthesis and study of polymers derived from metal-alkynyl building blocks (e.g., 1) an active area of research (4a–e). These materials hold the promise to



possess interesting electronic and structural properties; the encouraging discoveries of metal-alkynyl complexes and polymers that possess large nonlinear-optical responses (5), that are electrical conductors (6a–d), and that form liquid-crystal phases (7a–f) suggests that this will be a productive area of research for some time to come.

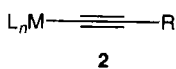
These diverse topics of study have more in common than their simple reliance on alkynyl ligands. A question of central importance to much of this field, and one for which a comprehensive answer has not yet been achieved, is: What is the nature of the bonding within the  $\text{M—C}\equiv\text{C—R}$  fragment? Or, stated more narrowly: Are metal-alkynyl bonds characterized by appreciable (or any)  $\text{M—CCR}$   $\pi$ -interactions, and, if so, for what metals, electron counts, ancillary ligands, and alkynyl R-groups? From the standpoint of the alkynyl-localized reactions of these compounds, understanding the electron distribution within the  $\text{C}\equiv\text{C}$  bond and the degree to which it is attenuated by the attached  $\text{ML}_n$  fragment are essential for rationalizing the relative electro- and nucleophilicity of the two carbon centers. Such questions are equally important to understanding the properties of the advanced materials that are derived from metal-alkynyl building blocks, because significant  $\pi$ -electron delocalization within the  $\text{M—C}\equiv\text{C—R}$  (or  $\text{M—C}\equiv\text{C—M}$ ) fragment is a prerequisite for the presence of large optical nonlinearities and electrical conductivities.

The question of potential  $M-CCR$   $\pi$ -bonding within the metal-alkynyl linkage arises from the simple frontier-orbital relationship between alkynyl ligands and the cyanide ligand, which is a known  $\pi$ -acceptor in some electronic environments (8). In fact, it was this simple analogy that motivated Nast to conduct his pioneering studies on metal-alkynyl complexes (1). A principal conclusion drawn from his spectroscopic and magnetic studies of a wide variety of high-symmetry metal-alkynyl complexes and ions from across the periodic table is that the cyanide and alkynyl ligands occupy similar positions in the spectrochemical series, lying toward the strong-field limit. The conventional interpretation of these data is that alkynyl ligands, like cyanide, are good  $\sigma$ -donors and modest  $\pi$ -acceptors (i.e., poorer than CO), as compared to other ligands within the series. Despite these early studies, the effort to refine this simple model and to understand the nature of metal-alkynyl bonding in fine detail has not kept pace with studies directed toward developing the synthetic, reaction, and materials-science chemistry of these complexes. Only a few of the many classes of metal-alkynyl complexes have been the subjects of theoretical calculations or detailed electronic- or photoelectron-spectroscopic studies, for example.

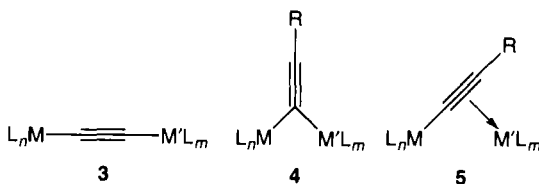
Until high-quality theoretical calculations and sensitive experimental probes of electronic structure are extended to the full range of metal-alkynyl complexes, any attempt to provide a general description of the nature of metal-alkynyl bonding is premature. In the absence of such a description, chemists have relied on the results of more readily accessible experimental techniques, especially X-ray crystallography and infrared spectroscopy, for insight into questions of electronic structure. [NMR spectroscopy is also an obvious probe of metal-alkynyl interactions; its applications in this regard have recently been reviewed (9).] In principle, the presence or absence of  $M-CCR$   $\pi$ -interactions in metal-alkynyl complexes should be manifested in  $M-C$  or  $C\equiv C$  bond distances and vibrational frequencies, with the latter potentially being highly sensitive probes by analogy to the textbook history of correlating the  $\nu(C\equiv N)$  and  $\nu(C\equiv O)$  frequencies of metal-cyanide and metal-carbonyl complexes with the extent of  $M \rightarrow CN$  and  $M \rightarrow CO$   $\pi$ -backbonding. Of course, there are other electronic factors, in addition to  $M-CCR$   $\pi$ -bonding, that influence the bond distances and vibrational frequencies within the  $M-C\equiv C-R$  fragment, so in order for these data to be properly interpreted it is essential that the limiting cases of metal-alkynyl bonding be clearly defined and that benchmark metrical and spectroscopic values corresponding to these cases be established. Despite the facts that hundreds of papers report vibrational spectroscopic and X-ray crystallographic data for metal-alkynyl complexes, and that these data have been widely invoked to

explain various aspects of metal-alkynyl bonding, this task has not, for the most part, been satisfactorily accomplished.

The purpose of this review is to attempt to discern, from consideration of the full range of data from these techniques, which metrical and vibrational-spectroscopic parameters may be meritoriously applied to the discussion of the electronic structures of metal-alkynyl complexes, and what conclusions may be drawn from them. Because this review aims to extract the intrinsic parameters that characterize  $M-C\equiv C-R$  bonding, the discussion is limited in scope to compounds possessing terminal ( $\eta^1$ ) alkynyl ligands bound to a single metal center (**2**); complexes, clusters, oligomers,



and polymers in which the bonding picture is complicated (albeit in interesting ways) because the alkynyl ligand bridges two or more metal centers, either in a  $\sigma$ -only or a side-on fashion (**3–5**), have, for the most part, been



excluded. In addition to the primary literature and review articles cited earlier on these clusters and polymers, a recent extensive review by Beck *et al.* on multimetallic compounds containing bridging hydrocarbyl ligands is noteworthy in this regard (10). The coverage of the literature extends into 1994 and is complete through 1993; where appropriate, there is overlap with Nast's review (1).

## II

### THEORETICAL AND EXPERIMENTAL BACKGROUND

We begin with a brief overview of the findings from the limited number of theoretical calculations, photoelectron and electronic-spectroscopic studies, and other physical measurements on terminal metal-alkynyl complexes in order to provide a context for discussing the results of X-ray

crystallographic and vibrational-spectroscopic studies. The simple analogy between cyanide and alkynyl ligands that seems to provide a reasonable framework for interpreting the results of Nast's work (1) has not always been upheld by the physical studies to be described below, both because the specific complexes in question vary among these studies, and because the various techniques employed in them are not equally sensitive (or successful) probes of metal-ligand interactions. As will become apparent, a single perspective on the nature of metal-alkynyl bonding cannot be distilled from this body of work.

### A. Molecular-Orbital Calculations and Photoelectron Spectroscopy

We describe the results from photoelectron-spectroscopic and molecular-orbital calculations together because these studies are frequently conducted in tandem. The primary conclusion from this work is that, in most of the complexes studied, the alkynyl ligand is good  $\sigma$ -donor and  $\pi$ -donor, but is a poor  $\pi$ -acceptor.

The first and most influential molecular-orbital calculation on metal-alkynyl complexes is that of Kostić and Fenske, who applied the Fenske-Hall method to the complexes  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{PH}_3)_2$  and  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{CO})_2$  (11). They concluded that the M-CCH bonds in these complexes are nearly pure  $\sigma$  in character. The large energy gap (ca. 15 eV) between the occupied metal orbitals and  $\pi^*(\text{C}\equiv\text{CH})$  levels severely limits the  $\pi$ -accepting quality of the latter, with the total electron population for the pair of  $\pi^*$  orbitals being  $0.22 e^-$  for  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{PH}_3)_2$  and  $0.14 e^-$  for  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{CO})_2$ . The filled  $\pi(\text{C}\equiv\text{CH})$  orbitals, in contrast, mix extensively with the higher-lying occupied metal orbitals; these filled-filled interactions result in the destabilization of the metal-based orbitals. The HOMOs of both complexes possess substantial coefficients at the alkynyl  $\beta$ -carbon; this was noted to be consistent with the alkynyl-localized reactivity of these complexes.

The conclusions of Kostić and Fenske for  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{CO})_2$  received firm experimental support a decade later from the work of Lichtenberger and co-workers, who carried out photoelectron-spectroscopic measurements and Fenske-Hall and extended-Hückel calculations on the complexes  $\text{FeCp}(\text{C}\equiv\text{CR})(\text{CO})_2$  ( $\text{R} = \text{H}, \text{Ph}, t\text{-Bu}, \text{C}\equiv\text{CH}$ ) and  $\text{FeCp}^*(\text{C}\equiv\text{C-Bu}')(\text{CO})_2$  (12a,b). Comparisons among the ionization energies of these compounds and to those of the methyl, chloro, and cyano derivatives of  $\text{FeCpX}(\text{CO})_2$ , as well as the nature of the vibronic structure observed in the spectra of  $\text{FeCp}(\text{C}\equiv\text{CH})(\text{CO})_2$  and  $\text{FeCp}(\text{C}\equiv\text{CBu}')(\text{CO})_2$ , led to several important conclusions. First, whereas cyanide stabilizes

$\pi$ -symmetry metal levels via  $\text{Fe} \rightarrow \text{CN} \pi$ -backbonding, the alkynyl ligands destabilize them as a result of  $\text{RCC} \rightarrow \text{Fe} \pi$ -donation. The extent of alkynyl  $\pi$ -donation depends strongly on the nature of the alkynyl R-group, being greater for the *t*-Bu, Ph, and  $\text{C}\equiv\text{CH}$  substituents than for the parent ethynyl ligand ( $\text{R} = \text{H}$ ). The  $\sigma$ -donor abilities of alkynyl ligands are also a function of R-group; among these  $\text{FeCpX(CO)}_2$  compounds,  $\sigma$ -donation by the X ligands increases according to  $\text{Cl} < \text{C}\equiv\text{CH}$ ,  $\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$ ,  $\text{C}\equiv\text{N} < \text{C}\equiv\text{CPh}$ ,  $\text{C}\equiv\text{CBu}' < \text{Me}$ . Overall, the interactions between the ethynyl ligand and the  $\text{FeCp(CO)}_2$  fragment are very similar to those of the chloride ligand with this metal center. The butadiynyl ligand ( $\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$ ) is described as being a better  $\pi$ -donor than halide ligands.

Photoelectron-spectroscopic studies by Oskam *et al.* on the series of *trans*-substituted complexes  $\text{M(C}\equiv\text{CR)}_2(\text{PEt}_3)_2$  ( $\text{M} = \text{Pd, Pt}$ ;  $\text{R} = \text{H, Me}$ ),  $\text{M(C}\equiv\text{N)}_2(\text{PEt}_3)_2$  ( $\text{M} = \text{Pd, Pt}$ ), and  $\text{Pd(C}\equiv\text{N)Cl(PEt}_3)_2$ , together with Hartree-Fock-Slater molecular-orbital calculations on the model  $\text{PH}_3$  derivatives, yielded a description of metal-alkynyl bonding that is essentially congruent with that for the  $\text{FeCp(C}\equiv\text{CR)(CO)}_2$  class of compounds:  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding is unimportant—the electron population of  $\pi^*(\text{CCR})$  is no greater than  $0.05 e^-$ —and net destabilizing interactions between the occupied  $\pi$ -symmetry metal and  $\pi(\text{CCR})$  orbitals are strong (13). However, in contrast to Lichtenberger's work (12*a,b*), which this study preceded, Oskam and co-workers concluded that the cyanide ligand is also a  $\pi$ -donor in these compounds, rather than a  $\pi$ -acceptor; thus, their work supports a cyano/alkynyl analogy, although not the traditional version that classifies these ligands as  $\pi$ -acceptors.

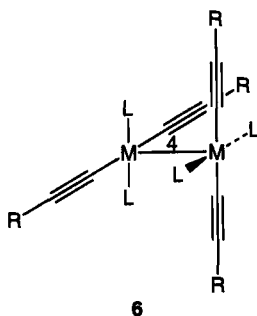
An exception to this picture of alkynyl ligands as  $\pi$ -donors is provided by Thompson and co-workers, who reported *ab initio* calculations on the  $d^0$  complexes  $\text{TiCp}_2(\text{C}\equiv\text{CR)}_2$  ( $\text{R} = \text{H, Me}$ ) (14). They noted that there is little evidence in their computational results for  $\text{RCC} \rightarrow \text{M} \pi$ -donation in these compounds, but that there is significant mixing between the alkynyl and Cp  $\pi$  levels. Unfortunately, attempts to measure photoelectron spectra of these compounds were unsuccessful.

## B. Electronic Spectroscopy

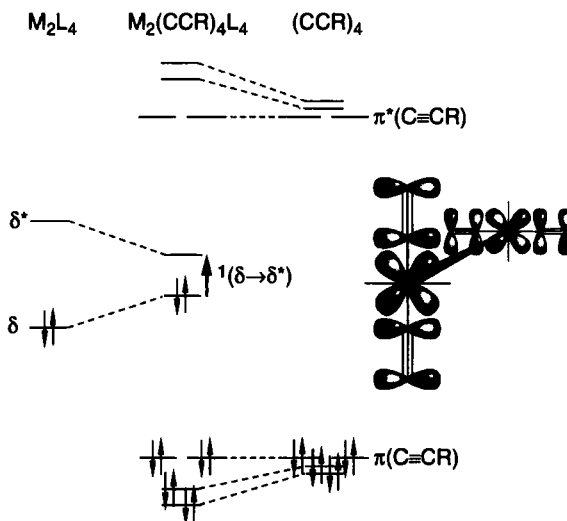
Electronic-absorption band maxima and extinction coefficients have been reported for a large number of metal-alkynyl complexes. In some papers, shifts in the energies of these bands within a class of  $\text{L}_n\text{M}-\text{CCR}$  complexes as a function of M, L, or R have been cited as indicating (or as being consistent with) the presence of  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding. Although qualitative assignments of electronic-absorption bands as arising

from generic  $d-d$ , charge-transfer, or  $\pi \rightarrow \pi^*$  transitions are not uncommon, with very few exceptions the experiments necessary to assign these bands definitively to transitions between specific orbitals or electronic and spin states have not been carried out (i.e., single-crystal polarized-light absorption measurements, cryogenic measurements for the observation of vibronic structure, and/or photophysical measurements). Casual comparisons of electronic-absorption band energies or intensities among a series of compounds in the absence of such experiments are not without the risk of misinterpretation because a variety of important effects not associated with the presence or absence of  $M-CCR$   $\pi$ -bonding may be operative, such as mixings between electronic states of identical symmetry but different orbital character. We limit our survey to those papers in which electronic transitions are assigned with some certainty, and that comment specifically on the nature of metal-alkynyl bonding.

Work in our laboratory directed toward developing a class of transition-metal complexes that are structurally and electronically analogous to conjugated organic compounds and polymers led to the synthesis and spectroscopic study of alkynyl-substituted, quadruply metal-metal bonded compounds of the type  $M_2(C\equiv CR)_4(PMe_3)_4$  (**6**;  $M = Mo, W$ ;  $R =$

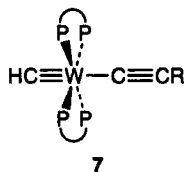


H, alkyl, Ph,  $SiMe_3$ ) (*15a-e*). These dimetallapolyynes compounds are particularly suitable for the study of metal-alkynyl  $\pi$ -interactions by electronic spectroscopy because the formally metal-metal localized  $\delta$  HOMO and  $\delta^*$  LUMO are of  $\pi$ -symmetry with respect to the alkynyl ligands, and hence the  ${}^1(\delta \rightarrow \delta^*)$  absorption band should manifest any  $M-CCR$   $\pi$ -interactions (Scheme 1). The  ${}^1(\delta \rightarrow \delta^*)$  transition energies of these alkynyl derivatives are substantially smaller ( $M = Mo$ ,  $\bar{\nu}_{max} = 13,500-15,500\text{ cm}^{-1}$ ), and their band intensities higher ( $\epsilon_{max} = 4500-9500\text{ M}^{-1}\text{ cm}^{-1}$ ), than those of  $Mo_2Cl_4(PMe_3)_4$  and  $Mo_2Me_4(PMe_3)_4$  ( $\bar{\nu}_{max} \cong 17,000\text{ cm}^{-1}$ ,  $\epsilon_{max} = 2000-3000\text{ M}^{-1}\text{ cm}^{-1}$ ). The red-shift and intensity of the  ${}^1(\delta \rightarrow \delta^*)$  band are dependent on the alkynyl R-group, increasing with

SCHEME 1 Frontier orbital interactions in  $M_2(CCR)_4(PMe_3)_4$  complexes.

the R-group  $\pi$ -conjugation according to  $R = H < \text{alkyl} < \text{SiMe}_3 < \text{Ph}$  (15*b,d*). These shifts parallel those of tetraalkynylethene compounds  $[(RC\equiv C)_2C=C(C\equiv CR)_2]$ , which are the organic analogues of the dimetallapolyynes (15*b*). The  $^1(\delta \rightarrow \delta^*)$  bands of the alkynyl complexes exhibit considerable vibronic structure, displaying progressions in the  $\nu(M^4-M)$ ,  $\nu(M-C)$ , and  $\nu(C\equiv C)$  modes. While these results (and complementary NMR (15*c*) and resonance Raman (15*d*) spectroscopic data) clearly indicate that significant  $M_2$ -CCR  $\pi$ -interactions are present in these complexes, the question of which alkynyl orbital(s) the metal  $\delta$  and  $\delta^*$  orbitals mix with [ $\pi(CCR)$  and/or  $\pi^*(CCR)$ ] cannot be addressed at this point. Nonetheless, these findings provide an interesting counterpoint to those from the photoelectron-spectroscopic studies of  $FeCp(C\equiv CR)(CO)_2$  (12*a,b*) in that the alkynyl ligands are decidedly not halidelike in their interactions with the frontier metal orbitals in these compounds.

We have also prepared and studied alkynyl-substituted methylidyne complexes of the type *trans*- $W(C\equiv CR)(\equiv CH)(dmpe)_2$  (7) (16*a-c*). Deducing the nature of the frontier orbital M-CCR  $\pi$ -interactions from the



lowest-energy electronic transition (assigned as  $[d_{xy} \rightarrow (d_{xz}, d_{yz})]$ ) of these metallabutadiynes is straightforward because only the  $(d_{xz}, d_{yz})$  levels are of  $\pi$ -symmetry with respect to the alkynyl ligand; the  $d_{xy}$  level is nonbonding. The transition energies of  $WX(\equiv CH)(dmpe)_2$  complexes lie in the order  $X = C\equiv CPh < C\equiv CSiMe_3 < C\equiv CH < n\text{-Bu (17)} < \text{halide (16a-c)}$ . The fact that the chloride and alkynyl derivatives exhibit opposing shifts of the  $[d_{xy} \rightarrow (d_{xz}, d_{yz})]$  band relative to the  $\sigma$ -only  $n$ -butyl derivative indicates that the alkynyl ligand is not acting as a  $\pi$ -donor toward the frontier orbitals to any significant extent in these compounds, but rather mixes strongly with the  $(d_{xz}, d_{yz})$  level via its  $\pi^*(CCR)$  orbitals. A recent extension of this study to include the cyanide derivative  $W(C\equiv N)(\equiv CH)(dmpe)_2$  reveals that the energy and intensity of its  $[d_{xy} \rightarrow (d_{xz}, d_{yz})]$  band are closely similar to those observed for the alkynyl derivatives (16c). The W-CCR bond lengths of the alkynyl compounds also appear to manifest a metal-alkynyl  $\pi$ -bonding interaction (Section III.C.1), as does the  $^1H$ -NMR spectrum of  $W(C\equiv CH)(\equiv CH)(dmpe)_2$ , which exhibits spin-spin coupling over five bonds between the ethynyl and methyldynyl hydrogen atoms.

The electronic spectra of complexes of the type *trans*- $M(C\equiv CR)_2L_2$  ( $M = Ni, Pd, Pt$ ) have been studied by several groups, and while experiments aimed at providing rigorous assignments for these spectra have not been undertaken, discussion of these studies is warranted by the considerable interest in the electronic properties of polymers derived from this class of compounds (4a,e). The absorption spectra of an extensive series of *trans*- $M(C\equiv CR)_2L_2$  ( $M = Ni, Pd, Pt$ ;  $R = H, Me, CH_2F, CH=CH_2, Ph, C\equiv CH, C\equiv CMe, C\equiv CPh$ ;  $L = PMe_3, PEt_3, SbEt_3$ ) complexes were reported by Masai *et al.* (18). The spectra are dominated by three intense ( $\epsilon \approx 10^4$ ) bands in the 200–350-nm region; no  $d-d$  bands were observed. The energy of the lowest-lying band is strongly dependent on the nature of the alkynyl R-group, red-shifting with increasing R-group conjugation (from  $R = H$  to  $C\equiv CPh$ ) by up to 0.5 eV, depending on  $M$  and  $L$ , and is linearly related to the first ionization potential of the free alkyne ( $HC\equiv CR$ ). Based on these data and a molecular-orbital calculation, Masai *et al.* concluded that the lowest-energy band arises from a transition between the  $\pi(CCR)$  and  $\pi^*(CCR)$  orbitals, with the transition possessing charge-transfer character as a result of mixing between the  $\pi^*(CCR)$  and metal  $(n + 1)p$ -orbitals. The R-group dependence of the transition energy was also interpreted as indicating that the  $RC\equiv C-M-C\equiv CR$  fragment is  $\pi$ -conjugated. Subsequent studies of the absorption spectra of polymers of the general class  $[M(C\equiv C-R-C\equiv C)(PR'_3)_2]_n$  ( $M = Ni, Pd, Pt$ ) by the Osaka group have yielded conclusions consistent with those for the monomeric compounds (7d,19).



The observation of luminescence from compounds containing the  $[\text{Pt}(\text{C}\equiv\text{CR})\text{L}_2]^+$  fragment is increasingly common (20–23), and vibronically structured emission spectra have been reported in several instances. DeGraff, Lukehart, Demas, and their coworkers discovered that the complexes  $\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PEt}_3)_2$  ( $\text{R} = \text{H}, \text{Ph}$ ) are intensely phosphorescent in glassy matrices at 77 K, and that the vibronic structure in the emission spectra consists primarily of a progression in the  $\nu(\text{C}\equiv\text{C})$  mode; the emission band of  $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$  exhibits additional progressions arising from phenyl-localized vibrational modes (21). The authors infer from these data that the emissive state is MLCT in character, with the excitation involving promotion of a metal electron to a  $\pi^*(\text{CCR})$  orbital. Although the authors did not reconcile their results with the photoelectron-spectroscopic data and molecular-orbital calculations of Oskam *et al.* on these compounds (13), the frontier-orbital scheme implied by this study is qualitatively consistent with Oskam's; the emission data shed no light on the question of  $\pi$ -bonding in the Pt–CCR linkage, however. Che *et al.* discovered that  $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2$  and  $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{Au}][\text{PF}_6]$  exhibit vibronically structured luminescence at 77 K similar to that observed for  $\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PEt}_3)_2$  (22). These data and extended-Hückel calculations on the model dmpm derivatives also suggest assignment of the emissive state as MLCT; the calculations indicate that  $\pi(\text{CCR}) \rightarrow \text{Pt } \pi$ -donation is important, and that  $\text{Pt} \rightarrow \pi^*(\text{CCR})$   $\pi$ -backbonding is not. Luminescence spectra of  $[\text{Pt}\{(\text{C}\equiv\text{C})_m\}_2(\text{PBu}_3^t)_2]_n$  polymers, reported by Lewis, Marder, Friend *et al.*, also exhibit vibronic structure similar to that for  $\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PEt}_3)_2$  (6b, 23), although these workers attributed the emission to an alkynyl-localized  $\pi\text{--}\pi^*$  excited state. Based on these data and complementary electronic-absorption spectroscopic studies, they concluded that the metal–alkynyl backbones of these polymers are  $\pi$ -conjugated.

### C. Other Physical Studies

The nature of metal–alkynyl bonding has been studied by a variety of other physical methods, although, as for the techniques described earlier, a single electronic model for this bond has not emerged. Experimental studies by Brindza, Bercaw, and co-workers of the relative Ru–X bond-dissociation energies within an extensive series of compounds of the type  $\text{RuCp}^*\text{X}(\text{PMe}_3)_2$  (24) revealed that ruthenium–carbon bond strengths decrease according to  $\text{Ru–CN} > \text{Ru–CCPh} > \text{Ru–C}(sp^3)$ . With few exceptions, the relative Ru–X energies are a linear function of the X–H bond strengths of the protonated free ligand. The fact that the relative Ru–CCPh bond strength fits this correlation would seem to imply that it is not

detectably strengthened by a Ru-C  $\pi$ -bonding component. In contrast, the Ru-CN bond is anomalously strong; this was interpreted as arising from substantial Ru  $\rightarrow$  CN  $\pi$ -backbonding. A related experimental study by Bercaw *et al.* on  $\text{ScCp}_2^*\text{X}$  complexes (25) showed that metal-carbon bond strengths decrease according to  $\text{Sc-CCR} > \text{Sc-C(aryl)} > \text{Sc-C(alkyl)}$ ; a similar conclusion has been reached through theoretical calculations (26).

From the results of  $^{57}\text{Fe}$  Mössbauer spectroscopy, Birchall and Myers concluded that the alkynyl ligand is a strong-field ligand, being a  $\sigma$ -donor and strong  $\pi$ -acceptor in ions of the type  $[\text{Fe}(\text{C}\equiv\text{CR})_6]^{4-}$  (27). In contrast, a study by Leigh *et al.* using this technique led to the conclusion that the alkynyl ligand is primarily a  $\sigma$ -donor in *trans*- $\text{Fe}(\text{C}\equiv\text{CPh})\text{X}(\text{L-L})_2$  ( $\text{X} = \text{Cl, Br; L-L} = \text{dmpe, depe}$ ) complexes (28).

Wrackmeyer, Sebal, and co-workers have conducted detailed multinuclear NMR-spectroscopic studies of metal-alkynyl complexes with the aim of probing the nature of the M-CCR bond; this work has been recently reviewed (9), so we mention only selected results. Germane to the discussion in the preceding sections is the conclusion that for *cis*- and *trans*- $\text{M}(\text{C}\equiv\text{CR})_2(\text{PR}'_3)_2$  ( $\text{M} = \text{Ni, Pd, Pt}$ ) complexes the  $^{13}\text{C}$  chemical shifts and  $^1J_{\text{C-H}}$  and  $^1J_{\text{C-C}}$  coupling constants (and, for the platinum complexes, the  $^{195}\text{Pt}$  chemical shifts and the  $^1J_{\text{Pt-C}}$  coupling constants) are consistent with the presence of  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding, with the extent of backbonding decreasing according to  $\text{Ni} > \text{Pd} > \text{Pt}$  (29). A  $^{19}\text{F}$ -NMR study by Parshall of the *m*- and *p*-fluorophenyl derivatives of *trans*- $\text{Pt}(\text{C}\equiv\text{CPh})(\text{C}_6\text{H}_4\text{F})(\text{PEt}_3)_2$  also indicated that the phenylethynyl ligand is a strong  $\pi$ -acceptor in these complexes (30). We have noted that the compounds  $1,1,2',2'\text{-W}_2(\text{C}\equiv\text{CMe})_2\text{Cl}_2(\text{PMe}_3)_4$  (15c) and *trans*- $\text{W}(\text{C}\equiv\text{CH})(\equiv\text{CH})(\text{dmpe})_2$  (16b) exhibit long range ( $\geq 5$  bonds) spin-spin couplings in their  $^1\text{H}$ -NMR spectra, as do their conjugated organic analogs, which is consistent with  $\pi$ -conjugation between their alkynyl and metal-centered multiple bonds.  $^1\text{H}$ -NMR spectroscopic studies of paramagnetic complexes by Köhler *et al.* on compounds of the type  $\text{VCp}'_2(\text{C}\equiv\text{CR})$  ( $\text{Cp}' = \text{Cp}$  or substituted  $\text{Cp}$ ;  $\text{R} = \text{aryl}$ ) (31a-c) and by Balch *et al.* on  $\text{Fe}(\text{TPP})(\text{C}\equiv\text{CPh})$  (31d) indicated that the unpaired metal-centered electron of these complexes is delocalized onto the alkynyl ligand, suggesting the presence of some type of M-CCR  $\pi$ -interaction. A contrasting picture is provided by Al-Najjar *et al.*, who reported that  $^{13}\text{C}$ -NMR data for  $[\text{Au}(\text{C}\equiv\text{CPh})\text{X}]^-$  ( $\text{X} = \text{Cl, Br, I, C}\equiv\text{CPh}$ ) ions are consistent with only weak  $\text{Au} \rightarrow \text{CCPh}$   $\pi$ -backbonding (32).

Electrochemical (primarily cyclic voltammetric) data have been reported for many metal-alkynyl complexes (33). In some studies, the redox potentials have been stated to be either consistent or inconsistent with

$M \rightarrow CCR$   $\pi$ -backbonding, depending on the complex, based on comparisons to electrochemical data for related halide, cyanide, or other compounds. We will not elaborate on these findings here, and note that such comparisons need not straightforwardly provide information about the nature of metal-alkynyl  $\pi$ -bonding because the redox-active orbitals probed by these measurements are not necessarily of  $\pi$ -symmetry with respect to the alkynyl ligand(s); in few of these studies are the orbitals involved in the electron-transfer process specifically identified. Solvation effects on electrochemical potentials also need to be accounted for if these data are to be treated as providing direct insight into orbital energies.

### III

#### X-RAY CRYSTALLOGRAPHIC STUDIES

##### A. Overview

The number of X-ray crystal structures of terminal metal-alkynyl complexes has increased ten-fold since the last review 13 years ago (1). Metrical data for the  $M-C\equiv C-R$  fragments of terminal metal-alkynyl complexes are set out in Table I (34-151). Bridging alkynyl complexes of the type  $L_nM-C\equiv C-ML_n$  (and higher  $L_nM-C_x-ML_n$  analogs) are not included in this survey; these complexes have been the subject of recent reviews (4b,10).

In addition to their obvious role in establishing connectivity and stereochemistry, the data from structural studies of metal-alkynyl complexes have been used to evaluate the  $M-C$  bond order, the extent of  $M \rightarrow CCR$   $\pi$ -backbonding and  $\pi$ -conjugation within the  $M-C\equiv C-R$  fragment, and the *trans* influences of alkynyl ligands. By analogy to the valence-bond canonical structures for metal-carbonyl complexes that represent the two limits of  $M \rightarrow CO$   $\pi$ -backbonding (8), the corresponding structures for metal-alkynyl complexes (9) suggest that the study of  $M-C$ ,  $C\equiv C$ , and



$C-R$  bond lengths is of particular importance for gaining insight into the nature of the metal-alkynyl bond. As will be described more fully later on, some of the structural perturbations of these linkages are subtle, and their observation thus requires high-quality X-ray diffraction data.

TABLE A  
METRICAL DATA FOR TERMINAL METAL-ALKYNYL COMPLEXES

Compound	$d(\text{M}-\text{C})$ (Å)	$d(\text{C}\equiv\text{C})$ (Å)	$d(\text{C}-\text{R})$ (Å)	$\angle(\text{M}-\text{C}\equiv\text{C})$ (°)	$\angle(\text{C}\equiv\text{C}-\text{R})$ (°)	Ref.
$\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\}_2(\text{C}\equiv\text{CSiMe}_3)_2$	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	177.0( <i>a</i> )	176.5( <i>a</i> )	(34)
$\text{ZrCp}_2(\text{C}\equiv\text{CMe})_2$	2.249(3)	1.206(4) <sup>b</sup>	1.462(5)	177.0(3)	179.4(4)	(35)
$\text{ZrCp}_2(\text{C}\equiv\text{CPh})\{\eta^2\text{-N(Ph)NHPh}\}$	2.258(6)	1.208(8) <sup>b</sup>	1.454(9)	179.0(7)	179.0(7)	(36)
$\text{ZrCp}(\text{C}\equiv\text{CBu}^t)(\text{CH}=\text{CHBu}^t)\text{Cl}(\text{dmpe})$	2.273(9)	1.20(1)	<sup>a</sup>	173.8(8)	<sup>a</sup>	(37)
$\text{VCp}_2(\text{C}\equiv\text{CBu}^t)$	2.075(5)	1.191(7) <sup>b</sup>	1.474(7)	177.0(4)	177.8(6)	(38)
$\text{V}(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2(\text{C}\equiv\text{CC}_6\text{H}_2\text{-1,3,5-Me}_3)$	2.032(13)	1.234(17)	1.447(14)	176.6(10)	175.5(12)	(31 <i>c</i> ,39)
<i>trans</i> - $\text{Mo}(\text{C}\equiv\text{CPh})_2(\text{dppe})_2$	2.093(8)	1.237(12)	1.422(12)	175.6(7)	177.8(9)	(33 <i>f</i> ,40)
$\text{Mo}(\text{C}\equiv\text{CBu}^t)(\text{H})_3(\text{dppe})_2$	2.175(10)	1.209(14)	1.458(15)	176.9(8)	177.1(11)	(41)
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CPh})(\text{dppe})$	2.138(5)	1.205(6) <sup>b</sup>	1.434(7)	178.5(4)	177.9(5)	(33 <i>g</i> )
$[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CPh})(\text{dppe})][\text{BF}_4]$	2.067(9)	1.196(11)	1.445(12)	174.6(8)	175.0(10)	(33 <i>g</i> ,42)
$\text{Mo}_2(\text{C}\equiv\text{CH})_4(\text{PMe}_3)_4$	2.153(4)	1.183(6) <sup>b</sup>	0.950(39)	171.7(3)	172.1(24)	(15 <i>b</i> )
	2.161(4)	1.174(6) <sup>b</sup>	0.909(35)	171.9(4)	166.7(24)	
	2.147(4)	1.203(5) <sup>b</sup>	1.471(6)	172.1(3)	177.6(4)	(15 <i>e</i> )
$\text{Mo}_2(\text{C}\equiv\text{CMe})_4(\text{PMe}_3)_4$	2.150(5)	1.888(7) <sup>b</sup>	1.469(9)	172.3(3)	178.4(5)	
	2.140(4)	1.195(5) <sup>b</sup>	1.473(6)	172.2(3)	178.8(6)	
	2.141(4)	1.195(6) <sup>b</sup>	1.471(6)	175.8(3)	176.9(4)	
	2.149(4)	1.199(7) <sup>b</sup>	1.473(7)	174.5(4)	178.1(4)	
	2.137(4)	1.185(6) <sup>b</sup>	1.465(8)	167.5(4)	178.5(6)	
	2.149(4)	1.198(6) <sup>b</sup>	1.476(6)	171.8(4)	176.8(4)	
	2.149(4)	1.193(5) <sup>b</sup>	1.474(5)	173.0(4)	178.1(5)	
	2.26(4)–	1.05(6)–	<sup>a</sup>	153(4)–	166(5)–	(15 <i>a</i> )
$\text{W}(\text{C}\equiv\text{CCO}_2\text{Me})_2(\text{H})_2(\text{dppe})_2$	2.49(4)	1.18(7)	<sup>a</sup>	164(4)	175(5)	
	2.038(21)	1.22(3)	1.40(4)	172.8(16)	168.5(23)	(33 <i>f</i> , <i>l</i> )
	2.041(25)	1.24(4)	1.41(6)	174.5(20)	175.9(24)	
$\text{W}(\text{C}\equiv\text{CPh})_2(\text{NPh})(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)_2$	2.148(15)	1.165(19)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(43)
	2.152(13)	1.165(17)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	
$\text{WCp}(\text{C}\equiv\text{C-}i\text{-Pr})(\text{CO})_2(\text{PMe}_3)$	2.134(11)	1.205(15)	1.417(18)	177.6(10)	176.8(13)	(44)

(continued)

TABLE I (continued)  
METRICAL DATA FOR TERMINAL METAL-ALKYNYL COMPLEXES

Compound	$d(\text{M}-\text{C})$ (Å)	$d(\text{C}\equiv\text{C})$ (Å)	$d(\text{C}-\text{R})$ (Å)	$\angle(\text{M}-\text{C}\equiv\text{C})$ (°)	$\angle(\text{C}\equiv\text{C}-\text{R})$ (°)	Ref.
<i>trans</i> -W(C≡CH)(CH)(dmpe) <sub>2</sub>	2.263(5)	1.192(8) <sup>b</sup>	0.822(68)	176.8(5)	179.5(56)	(16c)
<i>trans</i> -W(C≡CSiMe <sub>3</sub> )(CH)(dmpe) <sub>2</sub>	2.246(6)	1.228(9) <sup>b</sup>	1.814(7)	178.2(5)	179.8(7)	(16b)
<i>trans</i> -W(C≡CPh)(CH)(dmpe) <sub>2</sub>	2.250(4)	1.222(5) <sup>b</sup>	1.443(5)	171.6(3)	178.5(4)	(16c)
<i>trans</i> -W(C≡CC <sub>6</sub> H <sub>4</sub> -4-CCPr <sup>n</sup> )(CH)(dmpe) <sub>2</sub>	2.245(8)	1.210(11)	1.437(11)	178.2(7)	178.0(9)	(16c)
W <sub>2</sub> (C≡CMe) <sub>4</sub> (PMe <sub>3</sub> ) <sub>4</sub>	2.102(10)	1.203(15)	1.490(16)	174.3(10)	179.2(13)	(15e)
	2.121(12)	1.186(19)	1.473(22)	172.1(8)	177.1(10)	
	2.129(11)	1.217(16)	1.475(17)	172.1(9)	176.3(15)	
	2.129(11)	1.189(17)	1.474(19)	176.2(9)	178.5(10)	
	2.120(12)	1.183(17)	1.496(20)	174.9(10)	176.1(13)	
	2.124(10)	1.169(17)	1.495(21)	168.0(12)	175.8(13)	
	2.128(9)	1.176(13)	1.496(15)	173.3(11)	177.3(14)	
	2.139(11)	1.184(16)	1.497(17)	170.5(11)	178.3(11)	
1,1,2',2',-W <sub>2</sub> (C≡CMe) <sub>2</sub> Cl <sub>2</sub> (PMe <sub>3</sub> ) <sub>4</sub>	2.122(13)	1.213(19)	1.459(23)	173.1(11)	177.4(16)	(15c)
	2.141(12)	1.212(17)	1.441(20)	173.8(10)	174.1(15)	
<i>fac</i> -Mn(C≡CBu <sup>t</sup> )(dppe)(CO) <sub>3</sub>	1.996(6)	1.214(8) <sup>b</sup>	1.522(10)	179.0(5)	178.0(8)	(45)
<i>mer</i> -Mn(C≡CPh){P(OPh) <sub>3</sub> } <sub>2</sub> (CO) <sub>3</sub>	2.002(6)	1.198(9) <sup>b</sup>	1.450(8)	169.2(6)	177.7(7)	(46)
Mn(C≡CPPh <sub>3</sub> )Br(CO) <sub>4</sub>	1.981(14)	1.216(14)	1.679(13)	176.3(12)	164.0(12)	(47)
MnCp(C≡CPMe <sub>2</sub> Ph)(CO) <sub>2</sub>	1.895(5)	1.221(7)	1.683(6)	179.6(4)	166.6(5)	(48)
<i>fac</i> -Re(C≡CPh)(CO) <sub>3</sub> (py) <sub>2</sub>	2.108(9)	1.23(1)	1.42(1)	175(1)	178(1)	(49)
ReCp(C≡CMe)(NO)(PPh <sub>3</sub> )	2.066(7)	1.192(11)	1.484(12)	175.8(7)	176.8(9)	(50)
Re <sub>2</sub> (C≡CPh)(CO) <sub>7</sub> (μ-H)(μ-dmpm)	2.126(7)	1.200(9) <sup>b</sup>	1.432(9)	178.7(6)	178.9(6)	(51)
<i>trans</i> -Fe(C≡CMe) <sub>2</sub> (dmpe) <sub>2</sub>	1.968(6)	1.152(9) <sup>b</sup>	1.465(11)	<sup>a</sup>	<sup>a</sup>	(52a)
<i>trans</i> -Fe(C≡CPh) <sub>2</sub> (dmpe) <sub>2</sub>	1.925(6)	1.209(9) <sup>b</sup>	1.438(9)	<sup>a</sup>	<sup>a</sup>	(52a,b)
<i>trans</i> -Fe(C≡CPh) <sub>2</sub> (depe) <sub>2</sub>	1.918(3)	1.222(4) <sup>b</sup>	1.435(4)	<sup>a</sup>	<sup>a</sup>	(52a)
<i>trans</i> -Fe(C≡CC <sub>6</sub> H <sub>4</sub> -4-CCH) <sub>2</sub> (dmpe) <sub>2</sub>	1.933(3)	1.193(4) <sup>b</sup>	1.438(4)	<sup>a</sup>	<sup>a</sup>	(52a)
<i>trans</i> -Fe(C≡CPh)Cl(dmpe) <sub>2</sub>	1.897(3)	1.192(3) <sup>b</sup>	1.442(4)	178.4(2)	177.1(3)	(53)
<i>trans</i> -Fe(C≡CPh)Cl(dmpe) <sub>2</sub>	1.880(5)	1.216(8) <sup>b</sup>	1.421(8)	177.8(5)	177.5(6)	(54)
[ <i>trans</i> -Fe(C≡CMe)(C≡CHMe)(dmpe) <sub>2</sub> ][BPh <sub>4</sub> ]	1.963(7)	1.174(11)	1.467(14)	176.0(7)	177.7(9)	(55)

$[trans\text{-}Fe(C\equiv CPr^i)(C\equiv CHPr^i)(dmpe)_2][BPh_4]$	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(55)
$trans, cis\text{-}Fe[C\equiv CCH(OMe)_2]I[P(OMe)_3]_2(CO)_2$	1.948(4)	1.201(6) <sup>b</sup>	1.464(6)	170.7(5)	178.8(6)	(56)
$Fe(C\equiv CPh)\{P(CH_2CH_2PPh_2)_3\}$	1.92(1)	1.21(1)	1.45(1)	173.8(9)	174(1)	(33a)
$[Fe(C\equiv CPh)\{P(CH_2CH_2PPh_2)_3\}][BF_4]$	1.88(2)	1.20(3)	1.47(3)	175(2)	177(2)	(33a)
$FeCp(C\equiv CPh)(CO)_2$	1.920(6)	1.201(9) <sup>b</sup>	1.444(9)	174.4(4)	176.8(5)	(57)
$FeCp(C\equiv CPh)(dppm)$	1.900(7)	1.206(10) <sup>b</sup>	1.438(10)	177.4(7)	175.9(8)	(58)
	1.909(7)	1.201(10) <sup>b</sup>	1.430(10)	179.3(6)	177.4(8)	
$FeCp^*(C\equiv CH)(CO)_2$	1.921(3)	1.173(4) <sup>b</sup>	0.865(33)	178.70(26)	177.7(24)	(59)
$FeCp^*(C\equiv CPh)(CO)_2$	1.924(7)	1.214(9) <sup>b</sup>	1.431(9)	175.89(60)	175.46(70)	(59)
$[Ru(C\equiv CPh)(PMe_2Ph)_4][PF_6]$	2.051( <sup>a</sup> )	1.203( <sup>a</sup> )	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(60)
$trans\text{-}Ru(C\equiv CPh)_2(dppe)_2$	2.061(5)	1.207(7) <sup>b</sup>	1.434(7)	178.1(5)	174.4(6)	(61)
	2.064(5)	1.194(7) <sup>b</sup>	1.449(8)	174.3(5)	168.3(6)	
$trans\text{-}Ru(C\equiv CH)Cl(dppm)_2$	1.906(9)	1.162(9) <sup>b</sup>	0.899(0)	177.0(6)	180(0)	(62)
$trans\text{-}Ru(C\equiv CH)_2(CO)_2(PEt_3)_2$	2.078(1)	1.199(2) <sup>b</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(63a)
$trans\text{-}Ru(C\equiv CSiMe_3)_2(CO)_2(PEt_3)_2$	2.062(2)	1.221(2) <sup>b</sup>	1.812(2)	178.1(1)	176.1(1)	(63b)
$trans\text{-}Ru(C\equiv CPh)_2(CO)_2(PEt_3)_2$	2.074(3)	1.200(4) <sup>b</sup>	1.438(4)	<sup>a</sup>	<sup>a</sup>	(63a)
$trans\text{-}Ru(C\equiv CCCH)_2(CO)_2(PEt_3)_2$	2.078(2)	1.194(2) <sup>b</sup>	1.386(3)	177.9(1)	176.9(2)	(63b)
$trans\text{-}Ru(C\equiv CCCSiMe_3)_2(CO)_2(PEt_3)_2$	2.057(2)	1.226(2) <sup>b</sup>	1.370(2)	176.5(2)	178.9(2)	(63b)
$[cis, trans\text{-}Ru(C\equiv C\text{-}n\text{-}C_6H_{13})(CO)(py)_2(PPh_3)_2][ClO_4]$	2.01(3)	1.13(5)	1.54(5)	175(3)	171(5)	(64)
$[trans, mer\text{-}Ru(C\equiv CPh)(PPh_3)_2(CNBu^i)_3][PF_6]$	2.03(3)	1.17(4)	1.46(4)	175(3)	178(4)	(65)
$mer\text{-}Ru(C\equiv CPh)\{\eta^3\text{-}PhC\equiv CC\equiv CHPh\}$	2.037(3)	1.205(5) <sup>b</sup>	<sup>a</sup>	178.1(3)	<sup>a</sup>	(66a, b)
$\{PPh((CH_2)_3PCy_2)_2\}$						
$Ru(C\equiv CCO_2Me)\{OC(OMe)C\equiv CHCH=CHCO_2Me\}$ $(CO)(PPh_3)_2$	2.064(4)	1.203(5) <sup>b</sup>	1.444(6)	179.6(3)	168.2(5)	(67)
$Ru(C\equiv CPh)(CO)\{C_6H_3\text{-}3\text{-}Me\text{-}6\text{-}C(O)p\text{-}Tol\}$ $(PMe_2Ph)_2$	2.120(5)	1.192(7) <sup>b</sup>	1.432(7)	176.2(5)	178.9(6)	(68)
$RuCp(C\equiv CPh)(PPh_3)_2$	2.016(3)	1.215(4) <sup>b</sup>	1.456(4)	178.0(2)	171.9(3)	(69)
$RuCp(C\equiv CPh)(PPh_3)_2$	2.017(5)	1.214(7) <sup>b</sup>	1.462(8)	177.4(4)	170.6(5)	(70)
			1.418(8) <sup>c</sup>		170.6(5) <sup>c</sup>	
$RuCp\{C\equiv CC(OC(O)CF_3)=CMe_2\}(PPh_3)_2$	2.02(1)	1.20(1)	1.42(2)	175.1(11)	175.2(14)	(71)

(continued)

TABLE 1 (continued)  
METRICAL DATA FOR TERMINAL METAL-ALKYNYL COMPLEXES

Compound	$d(\text{M}-\text{C})$ (Å)	$d(\text{C}\equiv\text{C})$ (Å)	$d(\text{C}-\text{R})$ (Å)	$\angle(\text{M}-\text{C}\equiv\text{C})$ (°)	$\angle(\text{C}\equiv\text{C}-\text{R})$ (°)	Ref.
$\text{RuCp}\{\text{C}\equiv\text{CC}(\text{O})\text{Me}\}(\text{PPh}_3)_2$	1.996(3)	1.212(5) <sup>b</sup>	1.427(5)	176.1(3)	169.8(3)	(71)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{dppe})$	2.009(3)	1.204(5) <sup>b</sup>	1.444(5)	178.1(3)	176.3(4)	(72)
$(R, R)\text{-RuCp}(\text{C}\equiv\text{CPh})\{\text{PPh}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{PPh}_2\}$	2.038(7)	1.172(9) <sup>b</sup>	<sup>a</sup>	179.4(7)	172(1)	(70)
$\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\{\text{C}\equiv\text{CC}\equiv\text{CCPh}_2(\text{OSiMe}_3)\}(\text{PMe}_3)\text{Cl}$	1.93(3)	1.26(4)	1.40(5)	174(3)	175(4)	(73)
						(74)
$\text{Ru}_2\text{Cp}_2^*(\text{C}\equiv\text{C-}p\text{-Tol})_2(\mu\text{-SPr}^t)_2$	2.04(3)	1.16(4)	<sup>a</sup>	170(2)	<sup>a</sup>	(75)
	2.00(2)	1.14(4)	<sup>a</sup>	173(2)	<sup>a</sup>	
$\text{Ru}_2(\text{C}\equiv\text{CPh})_2\{\mu\text{-NC}_5\text{H}_4\text{-2-N}(\text{C}_6\text{F}_5)\}_4$	1.955(12)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(33c)
	1.951(11)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	
$\text{Ru}_2(\text{C}\equiv\text{CPh})(\mu\text{-NC}_3\text{H}_7\text{-2-NPh})_4$	2.08(3)	1.14(3)	1.51(3)	172(3)	173(3)	(33p)
$\text{Ru}_2(\text{C}\equiv\text{CPh})_2(\mu\text{-NPhCH}_2\text{NPh})_4$	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(33b)
<hr/>						
$\text{Os}(\text{C}\equiv\text{CCO}_2\text{Me})\{\text{OC}(\text{OMe})\text{CH}=\text{CH}\}(\text{CO})(\text{PPr}_i)_2$	1.977(4)	1.212(6) <sup>b</sup>	1.422(9)	176.9(4)	165.8(6)	(76)
			1.517(24) <sup>c</sup>		163.4(10) <sup>c</sup>	
$\text{Os}_3(\text{C}\equiv\text{CPh})(\text{CO})_6(\mu\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)_2(\text{NH}_2\text{Et})_2$	2.075(12)	<sup>a</sup>	<sup>a</sup>	178.3(6)	178.5(8)	(77)
	<sup>a</sup>	1.243(28)	1.494(31)	175.0(2)	177.3(22)	(78)
<i>trans, mer</i> - $\text{Co}(\text{C}\equiv\text{CPh})_2(\text{H})(\text{PMe}_3)_3$	<sup>a</sup>	<sup>a</sup>	1.548(33)	173.6(21)	173.1(25)	
$\text{Co}(\text{C}\equiv\text{CH})(\text{PMe}_3)_4$	1.890(6)	1.185(10) <sup>b</sup>	<sup>a</sup>	180.0(1)	<sup>a</sup>	(79)
$[\text{trans-Co}\{\text{C}\equiv\text{CCO}_2\text{Et}\}(\text{H})(\text{depe})_2][\text{BPh}_4]$	1.911(10)	1.192(15)	1.393(17)	176.2(9)	169.9(11)	(80)
<i>trans</i> - $\text{Co}(\text{C}\equiv\text{CSiMe}_3)\text{I}\{\text{N}_4\}$	1.948(5)	1.127(7) <sup>b</sup>	1.851(6)	175.3(5)	173.0(5)	(81)
$[\text{Co}(\text{C}\equiv\text{CSiMe}_3)(\text{H})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	178 <sup>(a)</sup>	(82)
$[\text{mer-Co}(\text{C}\equiv\text{CBu}^t)(\text{CH}=\text{CHBu}^t)(\text{NCMe})(\text{PMe}_3)_3][\text{BPh}_4]$	1.869(4)	1.209(6) <sup>b</sup>	1.476(6)	177.4(3)	178.6(4)	(83)
	1.857(12)	1.192(14)	1.358(15)	174(1)	178(1)	(84)
$\text{CoCp}(\text{C}\equiv\text{CCN})_2(\text{PPh}_3)$	1.877(7)	1.198(10) <sup>b</sup>	1.363(13)	173(1)	175(1)	
$\text{Rh}(\text{C}\equiv\text{CSiMe}_3)(\text{PMe}_3)_3$	2.02(1)	1.19(2)	1.79(2)	179.8(6)	176.5(5)	(85)
$\text{Rh}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_4$	2.002(3)	1.212(4) <sup>b</sup>	1.432(4)	178.0(1)	176.1(2)	(85)
$\{\text{Rh}(\text{PMe}_3)_4\}_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})$	2.014(4)	1.209(6) <sup>b</sup>	1.438(6)	177.3(4)	177.7(5)	(5b, 86a, b)
$\text{Rh}(\text{C}\equiv\text{CPh})(\eta^2\text{-C}(\text{CN})_2=\text{C}(\text{CN})_2)(\text{NCMe})(\text{PPh}_3)_2$	1.939(18)	1.179(28)	1.508(26)	174.6(17)	168.7(21)	(87)

[Rh(C≡CH)(H){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [BPh <sub>4</sub> ]	1.96(1)	1.20(2)	<sup>a</sup>	177(1)	<sup>a</sup>	(88a,b)
[cis-Rh(C≡CCH <sub>2</sub> CH <sub>2</sub> OH)(H)(PMe <sub>3</sub> ) <sub>4</sub> ]Cl	2.035(3)	1.196(4) <sup>b</sup>	<sup>a</sup>	178.5(5)	173.4(3)	(89)
trans,mer-Rh(C≡CPh) <sub>2</sub> (H)(PMe <sub>3</sub> ) <sub>3</sub>	2.019(4)	1.204(6) <sup>b</sup>	1.439(6)	173.9(2)	172.0(2)	(90)
	2.031(4)	1.213(6) <sup>b</sup>	1.440(6)	178.4(2)	178.3(3)	
{trans-Rh(C≡CSiMe <sub>3</sub> ) <sub>2</sub> (H)(dmpe)} <sub>2</sub> (μ-dmpe)	2.023(6)	1.200(9) <sup>b</sup>	1.810(7)	178.1(6)	175.3(6)	(90)
	2.031(6)	1.203(9) <sup>b</sup>	1.797(7)	176.9(5)	174.6(6)	
trans-Rh(C≡CSiMe <sub>3</sub> ) <sub>2</sub> (H)(py)(PPr <sub>3</sub> <sup>i</sup> ) <sub>2</sub>	2.032(6)	1.207(9) <sup>b</sup>	1.797(7)	177.0(5)	171.5(6)	(91)
	2.020(6)	1.219(9) <sup>b</sup>	1.801(7)	176.8(6)	167.5(6)	
Rh(C≡CCMe=CH <sub>2</sub> )(H)Cl(py)(PPr <sub>3</sub> <sup>i</sup> ) <sub>2</sub>	1.958(4)	1.206(5) <sup>b</sup>	1.432(6)	177.1(4)	176.1(5)	(92)
Rh <sub>2</sub> (C≡CH)(μ-NC <sub>5</sub> H <sub>4</sub> -2-NPh) <sub>4</sub>	2.021(10)	<sup>a</sup>	<sup>a</sup>	175.6(9)	<sup>a</sup>	(33i)
Ir(C≡CPh)(cod)(PCy <sub>3</sub> )	1.998(6)	1.200(10) <sup>b</sup>	1.447(11)	172.8(6)	176.5(8)	(93)
Ir(C≡CPh)(CO)(μ-dppm) <sub>2</sub> CuCl	2.04(1)	1.19(1)	1.46(1)	<sup>a</sup>	<sup>a</sup>	(94)
Ir(C≡CPh){C≡CC=C-1,2,3,4-(CO <sub>2</sub> Me) <sub>4</sub> }(CO)(PPh <sub>3</sub> ) <sub>2</sub>	2.056(9)	1.198(13)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(95)
Ir{C≡C(B <sub>10</sub> C <sub>2</sub> H <sub>11</sub> )}{CH=CH(B <sub>10</sub> C <sub>2</sub> H <sub>11</sub> )}Cl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1.99(2)	1.21(2)	1.40( <sup>a</sup> )	175(2)	175( <sup>a</sup> )	(96)
trans-Ni(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	1.87(1)	1.18(2)	1.46(2)	176.5(15)	176.5(15)	(97)
trans-Ni(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	1.879(11)	1.218(14)	1.464(15)	177.27(110)	176.92(133)	(98)
trans-Ni(C≡CC <sub>6</sub> H <sub>4</sub> -2-CCH) <sub>2</sub> (PBu <sub>3</sub> <sup>f</sup> ) <sub>2</sub>	1.859(17)	1.218(24)	1.469(24)	175.9(14)	178.9(16)	(99)
trans-Pd(C≡CSiMe <sub>3</sub> )Br(PPh <sub>3</sub> ) <sub>2</sub>	1.974(6)	1.16(1)	1.852(8)	175.0(6)	170.6(7)	(100)
{trans-PdCl(PEt <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> {μ-C≡CC(NPh)C(NPh)}	1.939(8)	1.200(12)	1.450(12)	176.8(9)	173.8(11)	(101)
trans-Pd(C≡CPh){C(CO <sub>2</sub> Me)=CH(CO <sub>2</sub> Me)}(PEt <sub>3</sub> ) <sub>2</sub>	2.04(2)	1.20(2)	1.47(2)	<sup>a</sup>	<sup>a</sup>	(102)
	2.03(2)	1.21(3)	1.41(3)	<sup>a</sup>	<sup>a</sup>	
trans-Pd(C≡CC <sub>6</sub> H <sub>4</sub> -2-CCH)(NCS)(PEt <sub>3</sub> ) <sub>2</sub>	1.952(7)	1.20(1)	1.46(1)	176(1)	174(1)	(103)
cis-Pd(C≡CSiMe <sub>3</sub> )Br(NMe <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -2-PPh <sub>2</sub> )	1.945(4)	1.193(6) <sup>b</sup>	1.834(4)	171.7(4)	172.3(4)	(104)
cis-Pd(C≡CPh) <sub>2</sub> (PPh <sub>3</sub> )Cl <sub>2</sub>	1.91(1)	1.23(2)	1.71(1)	175.5(9)	175.5(8)	(105)
trans-Pt(C≡CMe) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	2.062(8)	1.039(11)	1.541(13)	174.7(7)	173.5(9)	(106)
trans-Pt(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	1.98(1)	1.21(1)	1.43(1)	177.8(9)	176(1)	(107)
trans-Pt(C≡CC≡CPh) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub>	2.009(5)	1.175(8) <sup>b</sup>	1.406(8)	177.8(5)	177.1(6)	(5b,e)
trans-Pt(C≡CCMe=CH <sub>2</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.024(6)	1.18(1)	1.44(1)	177.4(5)	176.5(7)	(108)
trans-Pt(C≡CC <sub>6</sub> H <sub>4</sub> -4-OMe)(C≡CC <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub> )(PMe <sub>2</sub> Ph) <sub>2</sub>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(5f)

(continued)



TABLE I (continued)  
METRICAL DATA FOR TERMINAL METAL-ALKYNYL COMPLEXES

Compound	<i>d</i> (M–C) (Å)	<i>d</i> (C≡C) (Å)	<i>d</i> (C–R) (Å)	∠(M–C≡C) (°)	∠(C≡C–R) (°)	Ref.
<i>trans</i> -Pt(C≡CPh)Cl(PEt <sub>2</sub> Ph) <sub>2</sub>	1.98(2)	1.18(3)	1.44(3)	163(2)	174(2)	(109)
<i>trans</i> -Pt(C≡CCl)Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.933(12)	1.154(19)	1.690(15)	178(1)	<sup>a</sup>	(110)
<i>trans</i> -Pt(C≡CCMe=CH <sub>2</sub> )Cl(PPh <sub>3</sub> ) <sub>2</sub>	2.14(3)	1.09(4)	1.45(2)	151(3)	170(2)	(111)
<i>trans</i> -Pt(C≡CCMe=CH <sub>2</sub> )Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.84(2)	1.07(8)	1.59(8)	169(5)	178(2)	(112)
	1.88(6)	1.22(3)	1.52(3)	175(1)	173(6)	
<i>trans</i> -Pt{C≡CC(OH)Me <sub>2</sub> }Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.95(2)	1.18(2)	1.50(3)	175(1)	176(2)	(113)
<i>trans</i> -Pt{C≡CC(OH)MeEt}Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.988(9)	1.15(2)	1.52(2)	174(1)	178(1)	(113)
<i>trans</i> -Pt(C≡C- <i>c</i> -C <sub>6</sub> H <sub>10</sub> -1-OEt)Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.935(15)	1.22(2)	1.49(3)	172(1)	178(2)	(114)
<i>trans</i> -Pt{C≡CCMe <sub>2</sub> (OOH)}Br(PPh <sub>3</sub> ) <sub>2</sub>	1.990(9)	1.15(1)	1.49(1)	175.7(8)	173(1)	(115)
<i>trans</i> -Pt{C≡CCMeEt(OH)}(H)(PPh <sub>3</sub> ) <sub>2</sub>	1.90(1)	1.25(2)	1.58(4)	170(1)	169(2)	(116)
{ <i>trans</i> -Pt(NCS)(PEt <sub>3</sub> ) <sub>2</sub> }(μ-C≡CC <sub>6</sub> H <sub>4</sub> -4-C≡C)	1.921(12)	1.22(2)	1.45(2)	173(2)	178(2)	(117)
<i>trans</i> -Pt(C≡CBu')(CMe=CH <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2.04(1)	1.21(2)	1.46(2)	<sup>a</sup>	178(1)	(118)
<i>trans</i> -Pt(C≡CCMe=CH <sub>2</sub> ){C(CMe=CH <sub>2</sub> )=CH <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub>	1.99(1)	1.20(2)	1.46(2)	179(1)	178(2)	(119)
<i>trans</i> -Pt(C≡CPh){CPh=CH <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub>	1.99(2)	1.18(3)	1.48(2)	171(2)	176(2)	(120)
<i>trans</i> -Pt(C≡CMe){C(CMe=C(CN) <sub>2</sub> )=C- <i>c</i> -CH=CHC(=C(CN) <sub>2</sub> )CH=CH}{PMe <sub>3</sub> } <sub>2</sub>	2.009(15)	1.15(3)	1.54(3)	178.5(15)	175.9(20)	(121)
[ <i>trans</i> -Pt(C≡CBu')(PEt <sub>3</sub> ) <sub>2</sub> {C(1- <i>py</i> )=CHBu'}][SbF <sub>6</sub> ]	2.00(1)	1.20(2)	<sup>a</sup>	176(1)	178(2)	(122)
[ <i>trans</i> -Pt(C≡CPh)(NHNC <sub>6</sub> H <sub>4</sub> -4-F)(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	1.95(3)	1.21(5)	<sup>a</sup>	178( <sup>a</sup> )	172( <sup>a</sup> )	(123)
<i>cis</i> -Pt(C≡CH) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	1.987(15)	1.205(25)	<sup>a</sup>	178.7(17)	<sup>a</sup>	(124)
	1.949(16)	1.241(30)	<sup>a</sup>	178.1(16)	<sup>a</sup>	
<i>cis</i> -Pt(C≡CPh) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.10(3)	1.17(5)	1.48(4)	162(4)	169(4)	(125)
	2.04(3)	1.14(6)	1.48(6)	172(4)	171(5)	
	2.07(4)	1.21(5)	1.47(5)	165(4)	173(4)	
	2.02(4)	1.14(6)	1.43(5)	176(4)	173(5)	
<i>cis</i> -Pt{C≡CC(OH)Me <sub>2</sub> } <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.02(2)	1.17(2)	1.51(2)	177(2)	178(2)	(113)
	1.99(2)	1.19(2)	1.51(2)	178(1)	177(2)	
<i>cis</i> -Pt(C≡CCO <sub>2</sub> Me)(CO <sub>2</sub> Et)(PPh <sub>3</sub> ) <sub>2</sub>	1.991(8)	1.180(11)	1.434(13)	176.3(7)	174.3(9)	(126)

<i>cis</i> -Pt(C≡CCN)(CN)(PPh <sub>3</sub> ) <sub>2</sub>	1.96(3)	1.24(5)	1.31(5)	172.2(29)	173.7(37)	(127)
<i>cis</i> -Pt(C≡CBu')(CMe=CH <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1.97(2)	1.22(2)	1.46(2)	176(2)	175(2)	(128)
<i>cis</i> -Pt{C≡C(C <sub>5</sub> H <sub>4</sub> FeCp)} <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.010(11)	1.159(16)	1.485(17)	176.5(10)	<sup>a</sup>	(129)
	1.991(10)	1.139(16)	1.497(17)	174.5(10)	<sup>a</sup>	
<i>trans</i> -Pt(C≡C- <i>c</i> -C <sub>6</sub> H <sub>10</sub> -1-OH) <sub>2</sub> (H) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.004( <sup>a</sup> )	1.15( <sup>a</sup> )	1.55( <sup>a</sup> )	<sup>a</sup>	<sup>a</sup>	(130)
<i>cis,trans</i> -Pt(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> {N=NN=N-1,4-(C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub> )}	1.99(1)	1.20(2)	1.43(3)	172.5(9)	173(1)	(131)
Pt(C≡C- <i>p</i> -Tol)(μ-C≡C- <i>p</i> -Tol)(μ-dppm) <sub>2</sub> W(CO) <sub>3</sub>	2.00(1)	1.19(2)	1.47(2)	177.4(7)	175.0(2)	
[Pt(C≡CMe)(μ-C≡CMe)(μ-dppm) <sub>2</sub> Rh(CO)][PF <sub>6</sub> ]	2.000(8)	1.19(1)	1.45(1)	176.5(9)	<sup>a</sup>	(132a,b)
[Pt(C≡CMe)(μ-C≡CMe)(μ-dppm) <sub>2</sub> Rh(CO)][PF <sub>6</sub> ]	1.96(2)	1.13(3)	1.53(5)	175(2)	177(3)	(133)
<i>trans</i> -Pt(C≡CBu')(μ-C≡CBu'){(μ-dppm)AuCl} <sub>2</sub>	2.007(7)	1.211(10) <sup>b</sup>	1.491(11)	174.1(6)	175.5(8)	(134)
[Pt(C≡CBu')(μ-C≡CBu')(μ-dppm) <sub>2</sub> PtCl][ClO <sub>4</sub> ]	1.971(6)	1.194(9) <sup>b</sup>	<sup>a</sup>	177.3(4)	<sup>a</sup>	(20a)
Pt <sub>2</sub> (C≡CBu') <sub>2</sub> (μ-dppm) <sub>2</sub> (μ-AuI)	2.01(3)	1.14(3)	1.59(5)	172(2)	176(3)	(135)
	2.02(3)	1.10(3)	1.54(3)	177(2)	175(3)	
[{Pt(C≡CBu')} <sub>2</sub> (μ-C≡CBu')(μ-dppm) <sub>2</sub> ][BPh <sub>4</sub> ]	1.911(14)	1.231(23)	1.570(28)	175.4(13)	176.5(15)	(136)
	1.995(13)	1.195(20)	1.457(23)	175.5(13)	176.7(17)	
[{Pt(C≡CPh)} <sub>2</sub> (μ-C≡CPh)(μ-dppm) <sub>2</sub> ][ClO <sub>4</sub> ]	1.961(7)	1.18(1)	<sup>a</sup>	176.5(7)	178.8(6)	(20a)
[Pt(C≡CPh)(μ-N <sub>2</sub> C <sub>3</sub> Br <sub>3</sub> )(μ-dppm) <sub>2</sub> Rh(CO)][PF <sub>6</sub> ]	1.971(12)	1.177(17)	<sup>a</sup>	176.3(8)	<sup>a</sup>	(137)
[Pt(C≡C- <i>p</i> -Tol)(μ-dppm) <sub>2</sub> (μ-H)Ir{C≡C(C <sub>6</sub> H <sub>3</sub> Me)CH <sub>2</sub> CH=CHCH <sub>3</sub> }[BF <sub>4</sub> ]	1.985(14)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	179.0(11)	(138)
[ <i>trans</i> -Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> {μ-η <sup>2</sup> : η <sup>4</sup> -CPh=CC(Ph)-CH(Ph)}Pt(PEt <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	2.07(2)	1.11(2)	1.45(2)	177(1)	177(1)	(139)
[ <i>trans</i> -Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> {μ-η <sup>2</sup> : η <sup>4</sup> -CPh=CC( <i>p</i> -Tol)-CH( <i>p</i> -Tol)}Pt(PEt <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	1.96(2)	1.20(3)	1.45(4)	174(3)	170(3)	(140)
[Pt(C≡CBu')(PPh <sub>3</sub> ) <sub>3</sub> ][Au(PPh <sub>3</sub> ) <sub>6</sub> ][Au(C≡CBu') <sub>2</sub> ]	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(141)
[ <i>trans</i> -Pt(C≡CPh) <sub>2</sub> (μ-dppm) <sub>2</sub> Au][PF <sub>6</sub> ]	1.958(11)	1.23(2)	1.44(1)	174.0(9)	176(1)	(22)
	1.954(11)	1.23(2)	<sup>a</sup>	177(1)	<sup>a</sup>	
<i>trans</i> -Pt(C≡CPh) <sub>2</sub> (μ-dppm) <sub>2</sub> AgI	2.00(3)	1.22(4)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	(142)
	2.00(4)	1.20(5)	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	

(continued)

TABLE I (continued)  
METRICAL DATA FOR TERMINAL METAL-ALKYNYL COMPLEXES

Compound	$d(\text{M}-\text{C})$ (Å)	$d(\text{C}\equiv\text{C})$ (Å)	$d(\text{C}-\text{R})$ (Å)	$\angle(\text{M}-\text{C}\equiv\text{C})$ (°)	$\angle(\text{C}\equiv\text{C}-\text{R})$ (°)	Ref.
<i>trans</i> -Pt(C≡CPh)(PPh <sub>3</sub> ) <sub>2</sub> (μ-C≡CPh){ <i>cis</i> -Pt(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (CO)}	1.917(12)	1.206(18)	1.478(16)	176.7(12)	177.2(13)	(143)
Pt <sub>2</sub> (C≡CPh)(μ-C≡CHPh)(PEt <sub>3</sub> ) <sub>3</sub> Cl	2.045(16)	1.17(2)	1.45(2)	173.3(10)	178.3(19)	(20c)
Pt <sub>2</sub> (C≡CPh)(μ-C≡CHPh)(PEt <sub>3</sub> ) <sub>3</sub> I	2.012(10)	1.171(14)	1.475(14)	171.3(10)	178.4(10)	(20c)
[Pt <sub>2</sub> (C≡CPh)(μ-C≡CHPh)(PEt <sub>3</sub> ) <sub>4</sub> ][BF <sub>4</sub> ]	2.17(2)	1.14 <sup>(a)</sup>	<sup>a</sup>	163 <sup>(a)</sup>	172 <sup>(a)</sup>	(144)
Pt <sub>2</sub> (C≡CPh)(PCy <sub>3</sub> ) <sub>2</sub> (μ-C≡CPh)(μ-SiMe <sub>2</sub> )	2.01(1)	1.20(2)	1.43(2)	174(1)	174(1)	(145)
Au(C≡CPh)(PPh <sub>3</sub> )	1.97(2)	1.18(2)	1.46(2)	175.7(16)	176.5(18)	(146)
	2.02(2)	1.16(2)	1.47(2)	170.8(19)	174.0(20)	
Au(C≡CPh)(NH <sub>2</sub> Pr <sup>i</sup> )	1.935(19)	1.210(28)	1.479(28)	174.2(18)	178.6(21)	(147)
Au(C≡CC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> )	1.993(14)	1.197(16)	1.442(20)	175.4(10)	178.4(12)	(148)
Au(C≡CCH <sub>2</sub> OMe){P( <i>p</i> -Tol) <sub>3</sub> }	2.024(2)	1.169(3) <sup>b</sup>	1.474(4)	170.3(2)	178.2(3)	(149)
Au(C≡CBu <sup>i</sup> )(CNC <sub>6</sub> H <sub>3</sub> -2-Me-4-CCH)	1.955(10)	1.206(15)	1.463(16)	173.6(10)	173.9(12)	(150)
{Au(C≡CPh)} <sub>2</sub> {μ-PPt <sup>i</sup> <sub>2</sub> -4,4'-C <sub>6</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>4</sub> -PPt <sup>i</sup> <sub>2</sub> }	1.997(9)	1.179(11)	1.451(11)	172.7(9)	177.2(9)	(151)

<sup>a</sup> Not reported.

<sup>b</sup> Data included in Figure 2.

<sup>c</sup> Second datum due to disordered atom.

Examination of the data in Table I reveals that only one-third of the approximately 150 metal-alkynyl structures therein have been determined to a level of precision sufficient for meaningful discussions of the finer details of electronic structure; by our (admittedly arbitrary) definition, these are structures for which the estimated standard deviation (esd) for the  $\text{C}\equiv\text{C}$  bond distance is  $\leq 0.010$  Å. The dearth of precise structures is a reflection of the experimental difficulty, using X-ray diffraction methods, of locating light atoms that lie near a heavy-metal center. This point is well illustrated by the results of the two independent crystal-structure determinations for the complex *trans*- $\text{Fe}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dmpe})_2$ ; despite consistencies among the space group and unit cell dimensions, and the low *R*-factor to which each structure is refined, the  $\text{Fe}-\text{C}$ ,  $\text{C}\equiv\text{C}$  and  $\text{CC}-\text{C}(\text{Ph})$  bond distances reported in the two studies differ by 0.017, 0.024, and 0.021 Å, respectively (53,54). Not surprisingly, precise bond distances and bond angles are particularly uncommon for  $\text{M}-\text{C}\equiv\text{C}-\text{R}$  fragments of alkynyl complexes of third-row transition metals. We will confine our discussion to those metrical data with small esd's.

The following discussion centers on the electronic-structural implications of bond lengths within the  $\text{M}-\text{C}\equiv\text{C}-\text{R}$  fragments of metal-alkynyl complexes. We will not dwell on the bond angles within these subunits, and instead note at the outset that neither the  $\text{M}-\text{C}\equiv\text{C}$  nor the  $\text{C}\equiv\text{C}-\text{R}$  bond angle typically differs significantly from the expected  $180^\circ$ : The median for both angles is  $177^\circ$  among those structures for which the esd's  $\leq 1.0^\circ$ . Thus, these parameters appear to have little diagnostic value regarding the nature of metal-alkynyl bonding for complexes with terminal alkynyl ligands, other than to denote the  $\text{M}-\text{C}\equiv\text{C}-\text{R}$  unit as being alkyne-like. Small deviations from linearity for bond angles involving the  $\text{C}\equiv\text{C}$  fragment are not surprising in view of the fact that bending force constants of *sp*-hybridized carbon atoms are small compared to those for *sp*<sup>2</sup>- and *sp*<sup>3</sup>-hybridized carbon centers (152). Bending along the  $\text{M}-\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{C}-\text{R}$  coordinates has typically been interpreted as being the result of intermolecular interactions in the crystal, although specific crystal-packing details have rarely been presented. In principle, the structures—the  $\text{M}-\text{C}\equiv\text{C}-\text{H}$  bond angles, especially—of parent ethynyl complexes may additionally be susceptible to perturbation by an intermolecular interaction between the terminal hydrogen atom of the ethynyl ligand and the  $\text{C}\equiv\text{C}$  bond of an adjacent molecule. Such an arrangement is found for acetylene, which packs within the crystal in a T shape in which the  $\text{C}\equiv\text{C}$  axis of one molecule is roughly perpendicular to that of an adjacent one; the intermolecular  $\text{H}\cdots\text{C}$  distance is 2.74–3.39 Å, depending on temperature (153). At present, the only reported observation of a similar intermolecular arrangement of the CCH moieties of an ethynyl

complex is for  $\text{Mo}_2(\text{C}\equiv\text{CH})_4(\text{PMe}_3)_4$ , for which the  $\text{H}\cdots\text{C}\equiv\text{C}$  distance is 3.01 Å at 218 K (Figure 1) (15b).

### B. $\text{C}\equiv\text{C}$ Bond Distances

The  $\text{C}\equiv\text{C}$  bond distance has been invoked as a benchmark parameter for establishing the presence or absence of  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding in alkynyl complexes; bond distances both longer and shorter than “normal” (*vide infra*) have been taken as evidence for the  $\pi$ -acceptor character of alkynyl ligands. However, in metal–carbonyl complexes, only small differences (ca. 0.03 Å) in  $\text{C}\equiv\text{O}$  bond distances are observed among complexes for which the  $\text{C}\equiv\text{O}$  stretching frequencies (and hence, presumably, the magnitude of  $\text{M} \rightarrow \text{CO}$   $\pi$ -backbonding) vary significantly (154). Since carbon monoxide is unquestionably a stronger  $\pi$ -acceptor than are alkynyl ligands, the structural perturbation of the  $\text{C}\equiv\text{C}$  bond by  $\text{M}-\text{C}$   $\pi$ -bonding would not be expected to be large.

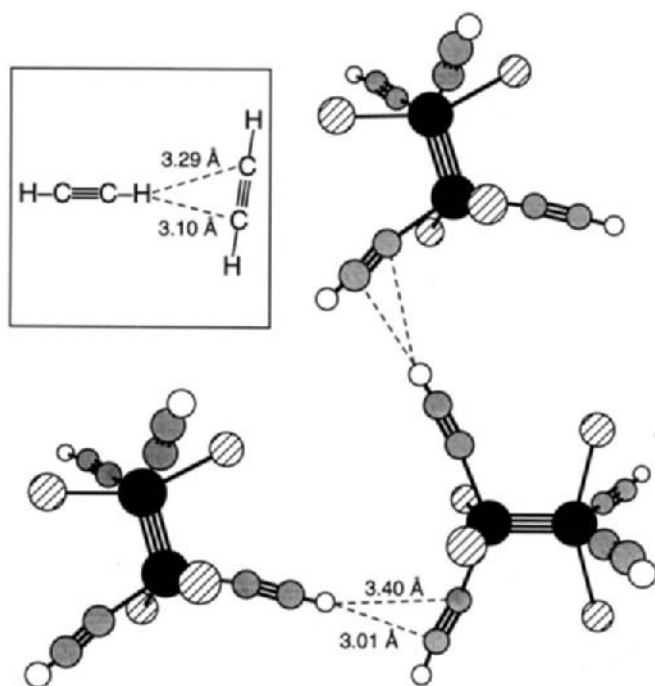


FIG. 1. Intermolecular interactions between ethynyl ligands of  $\text{Mo}_2(\text{C}\equiv\text{CH})_4(\text{PMe}_3)_4$  (15b). *Inset*: Intermolecular interactions in crystalline acetylene at  $T = 131$  K (153).

Displayed in Fig. 2 is the distribution of C≡C bond lengths for metal-alkynyl complexes in which the alkynyl R-group is hydrogen or is attached through a carbon or silicon atom; only C≡C bond lengths for which the esd is 0.010 Å or less are included. The distribution of C≡C distances is quite narrow, with two-thirds of them lying in the range 1.190–1.214 Å; the mean C≡C distance for substituted ( $L_nM-C\equiv C-C$  or  $L_nM-C\equiv C-Si$ ) compounds is 1.201(16) Å, where the standard deviation is that pertaining to the distribution, not the average of the crystallographic esd's (155). The C≡C bond lengths of trimethylsilylethynyl complexes [ $L_nM-C\equiv C-SiMe_3$ ;  $d(C\equiv C)_{\text{mean}} = 1.210(13)$  Å, ignoring the outlying point at 1.127 Å (81)] may be slightly longer than those of  $L_nM-C\equiv C-C(R)$  compounds, but there are too few data at present, and the distances are too widely distributed, to justify treating them separately from the latter complexes; in any case, removing them from the distribution does not change the mean C≡C bond length. Even fewer data are available for complexes of the parent ethynyl ligand [ $L_nM-C\equiv C-H$ ;

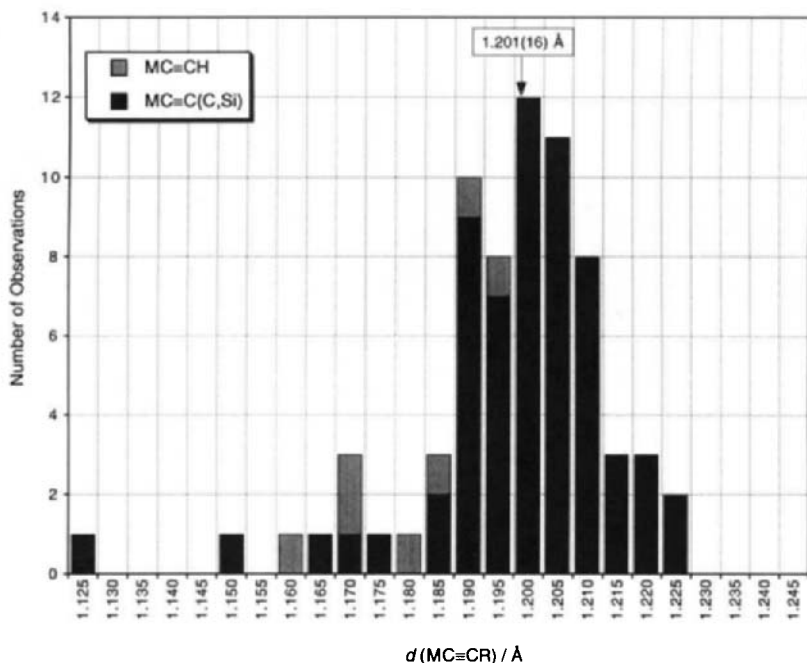


FIG. 2. Distribution of  $MC\equiv CR$  bond lengths (esd  $\leq 0.010$  Å). Data are taken from Table I. In structures where two C≡C bonds are identical under crystallographically imposed symmetry, only a single bond length is reported. The distance labels correspond to the left edges of the bins.

$d(\text{C}\equiv\text{C})_{\text{mean}} = 1.181(13) \text{ \AA}$ ], although reference to Fig. 2 suggests fairly strongly that the  $\text{C}\equiv\text{C}$  bonds of these compounds are shorter than those of substituted alkynyl complexes.

The logical way to interpret these bond lengths is to compare them to those of organic alkynes. In many papers, the reference point for what constitutes a "normal"  $\text{C}\equiv\text{C}$  bond distance is that of acetylene, which, at  $1.2033(2) \text{ \AA}$  [in the gas phase (156); other distances have been reported in crystallographic studies (153)], is nearly identical to the mean  $\text{C}\equiv\text{C}$  bond length for substituted metal-alkynyl complexes [ $1.201(16) \text{ \AA}$ ]. The bond length of the terminal alkyne ( $\text{HC}\equiv\text{CR}$ ) corresponding to the alkynyl ligand in question ( $\text{L}_n\text{M}-\text{C}\equiv\text{CR}$ ) is also a commonly used reference. However, a more meaningful interpretation of these data is afforded by establishing  $\text{C}\equiv\text{C}$  bond-length ranges for organic alkynes, and comparing these with the distribution of  $\text{C}\equiv\text{C}$  bond lengths in metal-alkynyl complexes. Figure 3 displays the distributions of  $\text{C}\equiv\text{C}$  bond lengths for organic alkynes of the type  $\text{HC}\equiv\text{CR}$  and  $\text{RC}\equiv\text{CR}'$  (where R is an organic substituent attached to the  $\text{C}\equiv\text{C}$  core through a carbon atom, and R' is attached through either a carbon or a silicon atom) whose crystal structures are recorded in the Cambridge Structural Database. These histograms include data only from crystallographically ordered, well-refined structures ( $R \leq 10\%$ ) for which the average esd of all carbon-carbon distances within the molecule is  $0.010 \text{ \AA}$  or less. As reported in an earlier compilation of the bond lengths of organic molecules (157), the mean  $\text{C}\equiv\text{C}$  bond distance for organic terminal alkynes [ $1.171(14) \text{ \AA}$ ] is shorter than that for disubstituted alkynes [ $1.192(12) \text{ \AA}$ ]; both distributions are narrow. Viewed in this context, it is apparent that the  $\text{C}\equiv\text{C}$  bonds of metal-alkynyl compounds are, in fact, slightly elongated (ca.  $0.01 \text{ \AA}$ ) relative to organic alkynes, and that the observation of shorter  $\text{C}\equiv\text{C}$  bonds for the parent metal-ethynyl compounds relative to substituted metal-alkynyl compounds ( $\text{L}_n\text{MCCR}$ ,  $\text{R} \neq \text{H}$ ) is consistent with the data for organic terminal and disubstituted alkynes. There are too few data for silyl-substituted alkynes to indicate whether their  $\text{C}\equiv\text{C}$  bonds are elongated relative to those of alkynes with a  $\text{C}-\text{C}\equiv\text{C}-\text{C}$  core, although, as for trimethylsilylethynyl metal complexes, there is a preliminary indication to that effect. These distributions also make clear that acetylene is an inappropriate reference compound because its gas-phase  $\text{C}\equiv\text{C}$  bond length is unusually long, and that comparing the  $\text{C}\equiv\text{C}$  bond lengths of terminal alkynes to those of substituted metal-alkynyl compounds is likely to significantly overestimate the elongation of the latter.

One possible explanation for the generally longer  $\text{C}\equiv\text{C}$  bonds of metal-alkynyl complexes relative to organic alkynes is that they are the result of  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding [or  $\text{RCC} \rightarrow \text{M} \pi$ -bonding, as could be

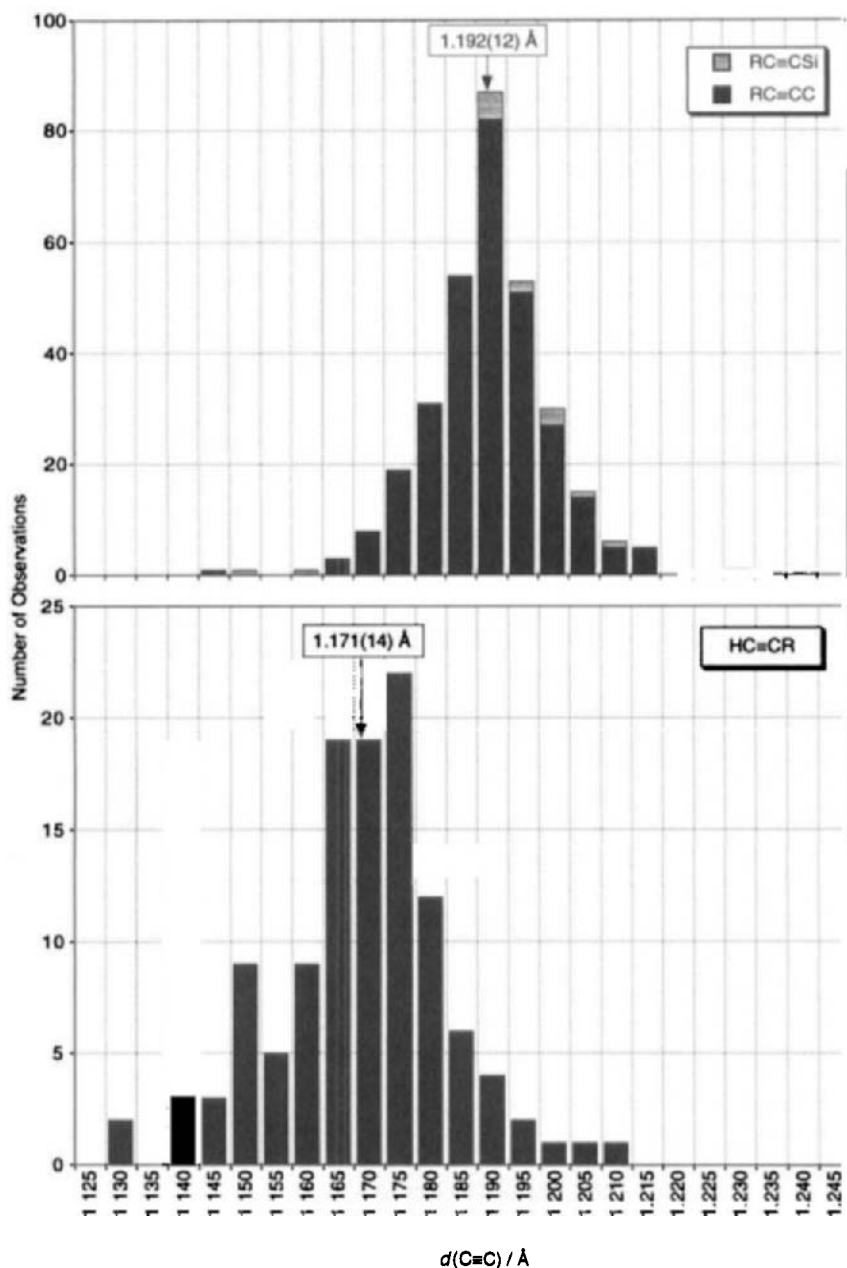


FIG. 3. Distributions of  $C\equiv C$  bond lengths ( $\text{esd} \leq 0.010 \text{ \AA}$ ) in organic terminal ( $RC\equiv CH$ ) and disubstituted ( $RC\equiv CR$ ,  $RC\equiv CR'$ ) alkynes. Data are taken from the Cambridge Structural Database. In structures with two or more crystallographically identical  $C\equiv C$  bonds, only a single bond length is included. Two outlying bond distances, at 1.12 and 1.36 Å, are not shown in the top figure. The distance labels correspond to the left edges of the bins.



inferred from the results of photoelectron-spectroscopic studies (12–13)]. Unfortunately, the narrow range of C≡C bond lengths, and their large individual uncertainties, makes this hypothesis essentially impossible to test via comparisons among  $L_nM$ -CCR complexes for which the  $ML_n$  fragments possess different  $d$ -electron counts or  $\pi$ -basicities, because, at the 3 $\sigma$  confidence level, nearly all C≡C bond lengths for the compounds in Fig. 2 are indistinguishable, and some of those that are statistically distinct from one another lack an obvious chemical reason for being so [e.g.,  $d(C\equiv C) = 1.152(9)$  Å for  $Fe(C\equiv CMe)_2(dmpe)_2$ ;  $d(C\equiv C) = 1.222(4)$  Å for  $Fe(C\equiv CPh)_2(depe)_2$ ] (52a). The sensitivity of the C≡C bond length to subtle differences in metal-alkynyl bonding is clearly very low, so small differences among these distances must be interpreted with caution. On a positive note, the extreme narrowness of the C≡C bond-length distribution suggests that bond lengths that clearly lie outside this range could be viewed as substantive evidence for significant M-CCR  $\pi$ -interactions. The only structural study to date that has provided compelling evidence for elongated C≡C bonds is that of Carty and co-workers for complexes of the type *trans*- $Ru(C\equiv CR)_2(CO)_2(PEt_3)_2$  ( $R = H, Ph, SiMe_3, C\equiv CH, C\equiv CSiMe_3$ ) (63a,b). Long C≡C bonds are observed in the structures of the complexes for which  $R = SiMe_3$  [1.221(2) Å] and  $C\equiv CSiMe_3$  [1.226(2) Å]. Corresponding contractions of the Ru-C bonds are also observed (Section III.C.3), consistent with multiple-bond character in these linkages.

An alternative explanation for the 0.01-Å elongation of metal-alkynyl C≡C bonds relative to those of organic alkynes is that they are the result of metal-carbon  $\sigma$ -bonds that are polarized in a  $M^{\delta+}-C^{\delta-}$  fashion. The lone pair of the alkynyl anion,  $[C\equiv CR]^-$ , is slightly C≡C  $\sigma$ -antibonding in character; significant residual negative charge on the alkynyl ligand could thus result in a longer-than-normal C≡C distance. An upper limit to the bond-length elongation due to this effect is provided by the C≡C distance of the free ethynyl anion,  $[C\equiv CH]^-$ . *Ab initio* molecular-structure calculations on this ion yield  $d(C\equiv C) = 1.2463(10)$  Å (158), which is ca. 0.04 Å longer than the C≡C bond of acetylene [1.2033(2) Å] (156), and ca. 0.08 Å longer than the average bond length of organic terminal alkynes [1.171(14) Å, Fig. 3]; these same calculations predict correctly the experimentally observed vibrational frequencies of this ion (159), suggesting that the calculated bond distance is a reliable one. While the  $M^{\delta+}-C^{\delta-}$  bond-polarity effect undoubtedly contributes to the general bond-length elongation of metal-alkynyl complexes, it is unlikely that it alone accounts for the long C≡C bonds observed for complexes such as *trans*- $Ru(C\equiv CR)_2(CO)_2(PEt_3)_2$  (63a,b) given that this is far from being the most electropositive metal center among those whose distances are

represented in Fig. 2. The  $\text{C}\equiv\text{C}$  bond lengths of alkali or alkaline-earth metal-alkynyl compounds would seem to be logical reference compounds to test this point. Unfortunately, nearly all either are polymeric or involve both  $\sigma$ - and  $\pi$ -type metal-carbon interactions.

### C. M-C Bond Distances

As is the case for transition-metal carbonyl complexes (154), the M-C bond distance should be a more sensitive structural indicator of the nature of the M-CCR bond than is the length of the multiple bond, because bond distances change more between bond orders 1 and 2 than between bond orders 2 and 3. As for the  $\text{C}\equiv\text{C}$  bond lengths described earlier, classifying a M-CCR bond length as "normal" or "short" requires a reference point; some approaches to this are described next.

#### 1. Comparisons to Metal-Alkyl Compounds

The best and simplest means of placing the M-C bond distances of metal-alkyl complexes in a context that allows insight into whether or not they manifest M-CCR  $\pi$ -interactions is to compare them to M-C bond distances of complexes where such effects are expected to be insignificant, as for metal-alkynyl compounds. For these comparisons to be most meaningful, the pair of complexes under consideration should obviously be closely similar with respect to oxidation state, overall charge, geometry, and ancillary ligands. Differences in M-C bond distances between alkynyl and alkyl complexes also need to be corrected for the 0.08-Å difference between the single-bond covalent radii of  $sp$ - and  $sp^3$ -hybridized carbon atoms [ $r(\text{C}_{sp}) = 0.69 \text{ Å}$ ,  $r(\text{C}_{sp^3}) = 0.77 \text{ Å}$ ] (157); only in those cases where the bond-length difference exceeds 0.08 Å by a statistically significant amount would invoking a M-CCR  $\pi$ -bonding explanation appear to be justified. We emphasize these points because one widely cited study that concludes that alkynyl ligands participate in little or no  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding does so on the basis of comparisons between M-C bond distances of neutral alkynyl complexes and cationic carbonyl compounds, and the use of 0.60 Å (one-half the  $\text{C}\equiv\text{C}$  bond length) as the single-bond covalent radius for  $sp$ -hybridized carbon (69); this latter error has been repeated in a subsequent analysis (70).

A complication with this type of interpretation is that it is formally valid only if the M-C bonds of the alkynyl and alkyl complexes in question are of comparable covalency, because bonds become stronger with increasing ionic character. The electronegativity of carbon is a sensitive function of its hybridization [ $\chi(\text{C}_{sp}) = 2.99$ ,  $\chi(\text{C}_{sp^3}) = 2.48$ ; Pauling scale] (160); thus,

the M–C bond ionicities of analogous metal–alkyl and metal–alkynyl complexes will differ, perhaps significantly enough to be manifested structurally. There are several equations for estimating empirically the ionic character of a bond, due originally to Pauling, and, related to these, equations for correcting covalent bond lengths for ionic character (161), of which the earliest is the well-known formula of Schomaker and Stevenson [Eq. (1)] (162):

$$d(\text{A-B})_{\text{calc}} = r(\text{A}) + r(\text{B}) - 0.09[\chi(\text{A}) - \chi(\text{B})] \quad (1)$$

The successes and failures of this and related equations have been well documented (163); in no case are any claimed to be of more than qualitative significance. Although many of these relationships were developed from data for main-group compounds, their application is not limited to these species. For example, Labinger and Bercaw have advanced a classical electronegativity argument to explain the fact that M–H bonds are typically stronger than M–C(alkyl) bonds (164).

An updated version of the Schomaker-Stevenson equation, which was generated by fitting more accurate bond distances, is given in Eq. (2) (165):

$$d(\text{A-B})_{\text{calc}} = r(\text{A}) + r(\text{B}) - 0.07[\chi(\text{A}) - \chi(\text{B})]^2 \quad (2)$$

The problem with applying this or related equations to the calculation of M–C bond lengths for metal–alkynyl complexes of the type  $\text{ML}_n(\text{CCR})$  is that one typically knows neither  $r(\text{ML}_n)$  nor  $\chi(\text{ML}_n)$ , either or both of which may differ significantly from the tabulated values for bare M or  $\text{M}^{x+}$ . If, however, M–C distances for two  $\text{ML}_n\text{R}'$  ( $\text{R}' = \text{alkyl, alkynyl}$ ) complexes are available, then  $r(\text{ML}_n)$  can be factored out and the bond-length difference  $\Delta d(\text{M-C}) = [d(\text{M-C}_{sp^3}) - d(\text{M-C}_{sp})]$  can be expressed as a function of  $\chi(\text{ML}_n)$  [Eq. (3)]; if an experimental value of  $\Delta d(\text{M-C})$  for a pair of  $\text{ML}_n\text{R}'$  complexes gives a chemically reasonable value of  $\chi(\text{ML}_n)$ , then M–C  $\pi$ -bonding need not be invoked, even if  $\Delta d(\text{M-C})$  exceeds 0.08 Å.

$$\Delta d(\text{M-C})_{\text{calc}} = r(\text{C}_{sp^3}) - r(\text{C}_{sp}) - 0.07[\chi(\text{ML}_n) - \chi(\text{C}_{sp^3})]^2 + 0.07[\chi(\text{ML}_n) - \chi(\text{C}_{sp})]^2 \quad (3)$$

Figure 4 shows plots of the relationship between  $\Delta d(\text{M-C})_{\text{calc}}$  and  $\chi(\text{ML}_n)$ , as derived from Eq. (3), using several different values each for the electronegativities of alkynyl and alkyl ligands. One line is based on the Pauling electronegativities of  $\text{C}_{sp}$  ( $\chi = 2.99$ ) and  $\text{C}_{sp^3}$  ( $\chi = 2.48$ ) (160), which undoubtedly overestimate the difference between the ionic character of their respective M–C bonds for most pairs of alkynyl and alkyl ligands. The other lines are based on the group electronegativities (160,

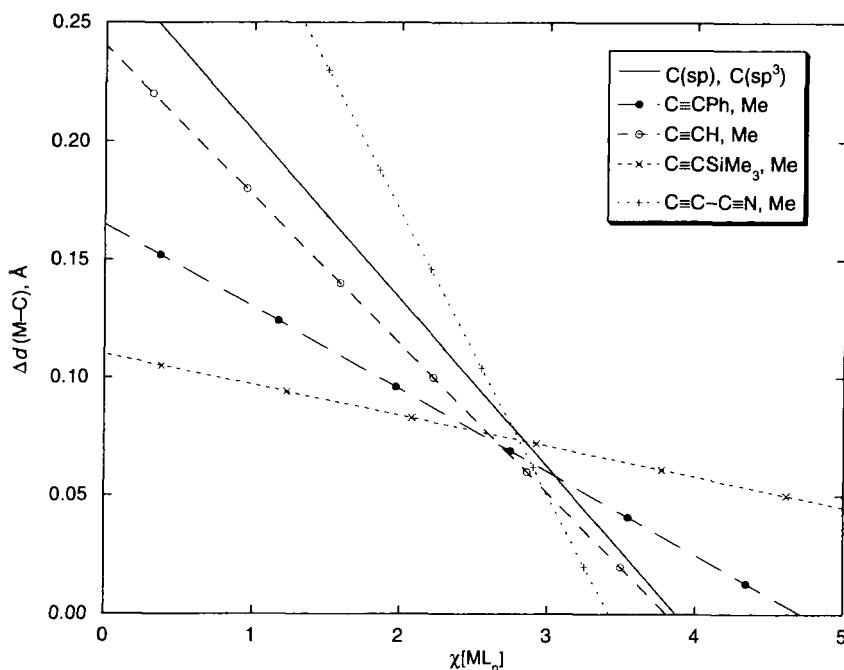


FIG. 4. Relationship between  $\Delta d(\text{M}-\text{C})$  and  $\chi(\text{ML}_n)$ , as provided by Eq. (3). The solid line is that obtained using the Pauling electronegativities for  $sp$ - and  $sp^3$ -hybridized carbon atoms; other lines are obtained using group electronegativities for the indicated ligands.

166) of specific alkynyl ligands [ $\chi(\text{C}\equiv\text{CH}) = 2.76$ ,  $\chi(\text{C}\equiv\text{CPh}) = 2.56$ ,  $\chi(\text{C}\equiv\text{CSiMe}_3) = 2.40$ ,  $\chi(\text{C}\equiv\text{CCN}) = 3.17$ ] and that of methyl ( $\chi = 2.31$ ); while the group electronegativities are probably more realistic than simply using  $\chi(\text{C}_{sp})$  and  $\chi(\text{C}_{sp^3})$  they too must be calculated, introducing yet another layer of approximation to the process. Different lines could be generated using electronegativities for other alkyl groups, other bond-distance-bond-ionicity equations, or other electronegativity scales. We wish to emphasize clearly that our choice of Eq. (2) and its associated parameter sets is based neither on a strong conviction that they are generally correct nor on independent evidence that they treat  $\text{M}-\text{C}$  bond lengths appropriately; we present these correlations only as one means by which  $\text{M}-\text{C}$  bond-length data may be interpreted, and to encourage discussion along these lines in future papers on metal-alkynyl structural chemistry.

Collected in Table II (167-176) are the  $\text{M}-\text{C}$  bond lengths ( $\text{esd} \leq 0.010 \text{ \AA}$ ) for  $\text{ML}_n(\text{CCR})$  metal-alkynyl complexes for which an analogous  $\text{ML}_n\text{R}'$  ( $\text{R}' = \text{alkyl}$ ) complex has also been structurally characterized.

TABLE II  
METAL–CARBON BOND LENGTHS FOR ANALOGOUS METAL–ALKYL AND METAL–ALKYNYL COMPLEXES

Metal–alkyl complex	$d(\text{M–C})^a$ (Å)	Ref.	Metal–alkynyl complex	$d(\text{M–C})^a$ (Å)	Ref.	$\Delta d^b$ (Å)
ZrCp <sub>2</sub> Me <sub>2</sub>	2.277[5]	(167)	ZrCp <sub>2</sub> (C≡CMe) <sub>2</sub>	2.249(3)	(35)	0.03
Mo <sub>2</sub> Me <sub>4</sub> (PMe <sub>3</sub> ) <sub>4</sub>	2.245[4]	(168)	Mo <sub>2</sub> (C≡CH) <sub>4</sub> (PMe <sub>3</sub> ) <sub>4</sub>	2.157[4]	(15b)	0.09
			Mo <sub>2</sub> (C≡CMe) <sub>4</sub> (PMe <sub>3</sub> ) <sub>4</sub>	2.145[4]	(15e)	0.10
<i>trans</i> -W(Bu <sup>n</sup> )(CH)(dmpe) <sub>2</sub>	2.405(6)	(17)	<i>trans</i> -W(C≡CH)(CH)(dmpe) <sub>2</sub>	2.263(5)	(16c)	0.14
			<i>trans</i> -W(C≡CPh)(CH)(dmpe) <sub>2</sub>	2.250(4)	(16c)	0.16
			<i>trans</i> -W(C≡CSiMe <sub>3</sub> )(CH)(dmpe) <sub>2</sub>	2.246(6)	(16b)	0.16
			<i>trans</i> -W(C≡CC <sub>6</sub> H <sub>4</sub> -4-CCPr <sup>n</sup> )(CH)(dmpe) <sub>2</sub>	2.245(8)	(16c)	0.16
<i>fac</i> -Mn{CH <sub>2</sub> SiMe(CH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> }(CO) <sub>3</sub>	2.198(5)	(169)	<i>fac</i> -Mn(C≡CBu <sup>i</sup> )(dppe)(CO) <sub>3</sub>	1.996(6)	(45)	0.20
<i>mer</i> -Mn{P(OPh) <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> -2-CH <sub>2</sub> )} {P(OPh) <sub>3</sub> }(CO) <sub>3</sub>	2.207(4)	(170)	<i>mer</i> -Mn(C≡CPh){P(OPh) <sub>3</sub> }(CO) <sub>3</sub>	2.002(6)	(46)	0.21
Fe(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> PPh <sub>2</sub> (WCpMe(CO) <sub>2</sub> ))Me(CO) <sub>2</sub>	2.06(1)	(171)	FeCp(C≡CPh)(CO) <sub>2</sub>	1.920(6)	(57)	0.14
			FeCp*(C≡CH)(CO) <sub>2</sub>	1.921(3)	(59)	0.14
			FeCp*(C≡CPh)(CO) <sub>2</sub>	1.924(7)	(59)	0.14
(S <sub>Ru</sub> , R <sub>C</sub> )-RuCpMe(PPh <sub>2</sub> CHMeCH <sub>2</sub> PPh <sub>2</sub> )	2.169(6)	(172)	RuCp(C≡CPh)(PPh <sub>3</sub> ) <sub>2</sub>	2.016(3)	(69)	0.15
			RuCp(C≡CPh)(dppe)	2.009(3)	(70)	0.16
			RuCp{C≡CC(O)Me}(PPh <sub>3</sub> ) <sub>2</sub>	1.996(3)	(72)	0.17
Co(η <sup>5</sup> -C <sub>5</sub> H <sub>2</sub> Me <sub>3</sub> )Me <sub>2</sub> (PPh <sub>3</sub> )	1.997(5)	(173)	CoCp(C≡CCN) <sub>2</sub> (PPh <sub>3</sub> )	1.867[10]	(84)	0.13
<i>cis</i> -PdMe <sub>2</sub> (tmeda)	2.028[3]	(174)	Pd(C≡CSiMe <sub>3</sub> )Br(NMe <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -2-PPh <sub>2</sub> )	1.945(4)	(104)	0.08
<i>trans</i> -PtMeCl(PPh <sub>3</sub> ) <sub>2</sub>	2.08(1)	(175)	<i>trans</i> -Pt{C≡CC(OH)MeEt}Cl(PPh <sub>3</sub> ) <sub>2</sub>	1.988(9)	(113)	0.09
Au{CH <sub>2</sub> CH <sub>2</sub> C(O)Ph}(PPh <sub>3</sub> )	2.077(9)	(176)	Au(C≡CCH <sub>2</sub> OMe){P( <i>p</i> -Tol) <sub>3</sub> }	2.024(2)	(149)	0.05
			{Au(C≡CPh)} <sub>2</sub> (μ-PPri <sup>i</sup> -4,4'-C <sub>6</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>4</sub> PPri <sup>i</sup> )	1.997(9)	(151)	0.08

<sup>a</sup> Values in square brackets are the means of crystallographic esd's.

<sup>b</sup>  $\Delta d(\text{M–C}) = [d(\text{M–C}_{sp^3}) - d(\text{M–C}_{sp})]$ .

The paucity of available comparisons, despite the number of entries in Table I, is again testimony to the experimental difficulties that beset the determination of M–C bond lengths.

The first entry in Table II is in some respects the most intriguing. Erker and co-workers have reported a high-quality structure for  $\text{ZrCp}_2(\text{C}\equiv\text{CMe})_2$  (35), the Zr–C bond lengths of which [2.249(3) Å] are 0.03 Å shorter than those for  $\text{ZrCp}_2\text{Me}_2$  [2.277(5) Å] (167), where the value in parentheses is the average of the crystallographic *eds*'s. Since  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding is absent for these  $d^0$  systems, and theoretical calculations on the related complex  $\text{TiCp}_2(\text{CCH})_2$  indicate that the alkynyl ligand is not acting as a  $\pi$ -donor (14), the fact that  $\Delta d(\text{Zr}-\text{C})$  is significantly different from the pure single-bond value of 0.08 Å is surprising; that it is considerably *smaller* than 0.08 Å is striking under any circumstances. From bond-ionicity arguments (Fig. 4), the 0.03-Å difference between the lengths of the Zr–Me and Zr–CCMe bonds can be rationalized only if the group electronegativity of the  $[\text{ZrCp}_2\text{R}']$  fragment is  $>3.5$ ! While this value seems implausibly high, it finds some support in the observations of Labinger and Bercaw (164), who conclude from their study of metal–hydride and metal–alkyl bond strengths that the electronegativity of  $[\text{ScCp}_2^*]$  is quite high, being roughly equal to that of methyl. This pair of zirconium compounds represents the only case for which  $\Delta d(\text{M}-\text{C}) \ll 0.08$  Å; structural studies of other pairs of metal–alkynyl and metal–alkyl compounds from Group 3 or 4 would provide insight into the generality or singularity of this observation.

Studies in our research group on conjugated transition-metal compounds and polymers have resulted in the structural characterization of several quadruply metal–metal bonded dimetallapolyynes complexes of the type  $\text{M}_2(\text{C}\equiv\text{CR})_4(\text{PMe}_3)_4$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{R} = \text{H}, \text{alkyl}, \text{aryl}, \text{SiMe}_3$ ) (15a–e). The electronic, resonance-Raman, and NMR spectra of these species provide clear evidence for M–CCR  $\pi$ -interactions between the  $\text{M}_2$  core and the alkynyl ligands (Scheme 1, Section II-B). Comparison of the M–C bond lengths of  $\text{Mo}_2(\text{C}\equiv\text{CH})_4(\text{PMe}_3)_4$  [2.157(4) Å] (15b) and  $\text{Mo}_2(\text{C}\equiv\text{CMe})_4(\text{PMe}_3)_4$  [2.145(4) Å] (15e) with those of the analogous complex  $\text{Mo}_2\text{Me}_4(\text{PMe}_3)_4$  [2.245(4) Å] (168) yields  $\Delta d(\text{Mo}-\text{C})$  values of 0.09 Å and 0.10 Å, respectively (Table II). This indicates that the M–CCR  $\pi$ -interactions in these complexes are of insufficient magnitude to be manifested structurally. From Fig. 4, the group electronegativity of the  $[\text{Mo}_2\text{R}'_2(\text{PMe}_3)_4]$  fragment obtained from these values of  $\Delta d(\text{Mo}-\text{C})$  is 2.1–2.4; this compares favorably with  $\chi(\text{Mo}^{\text{II}}) = 2.19$  (160).

The class of metallabutadiene complexes of the type *trans*- $\text{W}(\text{C}\equiv\text{CR})(\equiv\text{CH})(\text{dmpc})_2$  ( $\text{R} = \text{H}, \text{SiMe}_3, \text{Ph}, \text{C}_6\text{H}_4\text{-4-CCPr}^n$ ) provides a second example from our laboratory for which there is strong spectro-

scopic evidence for metal-alkynyl  $\pi$ -conjugation (Section II-B). The W-C bond lengths of these complexes lie in the range 2.245(8)–2.263(5) Å (16a–c), and are considerably shorter [ $\Delta d(\text{W-C}) = 0.14\text{--}0.16$  Å, Table II] than the W-C<sub>sp</sub> bond length for *trans*-W(Bu<sup>n</sup>)(≡CH)(dmpe)<sub>2</sub> [2.405(6) Å] (17). This is consistent with the presence of a significant  $\pi$ -bonding component to the HCW-CCR linkage; a bond-ionicity interpretation for the 0.16-Å bond-length difference observed for the R = SiMe<sub>3</sub>, Ph, and C<sub>6</sub>H<sub>4</sub>-4-CCPr<sup>n</sup> derivatives unreasonably suggests  $\chi[\text{W}(\equiv\text{CH})(\text{dmpe})_2] \cong 0$  (Fig. 4), in the absence of M-CCR  $\pi$ -bonding (and steric effects for the *n*-Bu ligand). Consistent with this finding, the C≡C bond lengths of *trans*-W(C≡CPh)(≡CH)(dmpe)<sub>2</sub> [1.222(5) Å] (16c) and W(C≡CSiMe<sub>3</sub>)(≡CH)(dmpe)<sub>2</sub> [1.228(9) Å] (16b) are among the longest known for metal-alkynyl complexes (Table I), although, as noted in Section III-B, the interpretation of these data as being indicative of M-CCR  $\pi$ -bonding is not unambiguous.

The largest apparent contractions of metal-alkynyl bonds relative to metal-alkyl bonds are found for complexes of manganese. Comparison of the Mn-C bond lengths of the Mn<sup>I</sup> alkynyl complexes *fac*-Mn(C≡CBu')(dppe)(CO)<sub>3</sub> [1.996(6) Å] (45) and *mer*-Mn(C≡CPh){P(OPh)<sub>3</sub>}<sub>2</sub>(CO)<sub>3</sub> [2.002(6) Å] (46) with those of the alkyl complexes *fac*-Mn(CO)<sub>3</sub>{CH<sub>2</sub>SiMe(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}[2.198(5) Å] (169) and *mer*-Mn(CO)<sub>3</sub>{P(OPh)<sub>3</sub>}{P(OPh)<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>)}[2.207(4) Å] (170), respectively, gives  $\Delta d(\text{Mn-C}) \cong 0.20$  Å for both pairs of complexes (Table II). An unfortunate complication with this comparison is that the Mn-C bond distances of the alkyl reference compounds may be lengthened by ring strain, which would inflate  $\Delta d(\text{Mn-C})$ . There is no independent evidence of M → CCR  $\pi$ -backbonding from spectroscopic studies of these alkynyl complexes that would lead one to expect short Mn-C bonds for them.

The structures of complexes of the FeCpR'(CO)<sub>2</sub> type are worthy of mention because FeCp(C≡CR)(CO)<sub>2</sub> complexes are among the few alkynyl compounds to have been the subject of both theoretical calculations (11) and photoelectron-spectroscopic studies. (12a,b). The Fe-C bond lengths of the structurally characterized FeCp(C≡CR)(CO)<sub>2</sub> complexes (57,59) exhibit remarkable consistency (Table II), with an average Fe-CCR distance of 1.922 Å. Unfortunately, the 2.06(1)-Å Fe-C(Me) bond distance of Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(PPh<sub>2</sub>WCpMe(CO)<sub>2</sub>)}Me(CO)<sub>2</sub> (171), the alkyl reference compound, is not sufficiently precise to allow with any certainty the assessment of the nature of the Fe-CCR bonding in these compounds.

The series of related ruthenium complexes of the type RuCp(C≡CR)L<sub>2</sub> (R = Ph, L = PPh<sub>3</sub>, 1/2 dppe; R = C(O)Me, L = PPh<sub>3</sub>) (69,70,72), are more useful in this context. Comparison of the Ru-C bond distance of

$\text{RuCpMe}(\text{PPh}_2\text{CHMeCH}_2\text{PPh}_2)$  [2.169(6) Å] (172) with those of the alkynyl complexes yields  $\Delta d(\text{Ru}-\text{C}) = 0.15\text{--}0.17$  (Table II), which would appear to indicate that the Ru-C bond order of the alkynyl complexes is greater than 1; for  $\Delta d(\text{Ru}-\text{C})$  to be the result of bond-ionicity factors alone in the phenylethynyl complexes would require  $\chi[\text{RuCpL}_2] < 0.5$  (Fig. 4). The 0.02-Å difference between the Ru-C distances of the two  $\text{RuCp}(\text{C}\equiv\text{CR})(\text{PPh}_3)_2$  complexes [R = Ph, 2.016(3) Å; R = C(O)Me, 1.996(3) Å] might be interpreted as implying that this  $\pi$ -bonding is due to  $\text{Ru} \rightarrow \text{CCR} \pi$ -backbonding, since the CCC(O)Me ligand should be a better  $\pi$ -acceptor than CPh. However, the electronegativities of the two ligands are sufficiently different ( $\chi[\text{C}\equiv\text{CPh}] = 2.56$ ,  $\chi[\text{C}\equiv\text{CC(O)Me}] = 2.76$ ) that this need not be the case; for  $\text{RuCp}\{\text{C}\equiv\text{CC(O)Me}\}(\text{PPh}_3)_2$ , a group electronegativity for the  $[\text{RuCp}(\text{PPh}_3)_2]$  fragment of ca. 1.1 would account for  $\Delta d(\text{Ru}-\text{C}) = 0.17$  Å.

The cyanoethynyl ligand ( $\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ ) should be among the best of all alkynyl ligands in terms of potential  $\pi$ -acceptor character, both because of its large group electronegativity ( $\chi = 3.17$ ) and the viability of a  $\text{M}=\text{C}=\text{C}=\text{C}=\text{N}$  canonical structure. High-quality structural data are available for one metal complex of this ligand: The mean Co-C bond distance of  $\text{CoCp}(\text{C}\equiv\text{C}-\text{C}\equiv\text{N})_2(\text{PPh}_3)$  is 1.867(14) Å (84), which can be compared to that of  $\text{Co}\{\eta^5\text{-C}_5\text{H}_2\text{Me}_3\}\text{Me}_2(\text{PPh}_3)$  [1.997(5) Å] (173) to yield  $\Delta d(\text{Co}-\text{C}) = 0.13$  Å (Table II). This might be taken as evidence for the presence of a significant Co-C  $\pi$ -bonding interaction. However, the large electronegativity of CCCN also implies that the difference between the M-C bond ionicities of complexes of this ligand and analogous metal-alkyl complexes will be greater than for other pairs of metal-alkynyl and metal-alkyl complexes. Reference to Fig. 4 indicates that, for this ligand, a M-C bond-length contraction of 0.15 Å corresponds to  $\chi[\text{CoCpR}'(\text{PPh}_3)] = 2.2$ ; this is in reasonable agreement with the value for  $\text{Co}^{\text{II}}$  ( $\chi = 1.88$ ) (160). Unfortunately, the  $\text{C}\equiv\text{C}$ ,  $\text{CC}-\text{CN}$ , and  $\text{C}\equiv\text{N}$  distances of this compound are not of sufficiently high precision to provide insight into whether the large M-C bond contraction seen for this compound is the result of  $\pi$ -backbonding.

Among the alkynyl complexes of Groups 9 and 10, there are no examples at present for which there is structural evidence for M-C  $\pi$ -bonding; the compounds  $\text{Pd}(\text{C}\equiv\text{CSiMe}_3)\text{Br}(\text{NMe}_2\text{CH}_2\text{C}_6\text{H}_4\text{-2-PPh}_2)$  (104,177), *trans*- $\text{Pt}\{\text{C}\equiv\text{CC(OH)MeEt}\}\text{Cl}(\text{PPh}_3)_2$  (113),  $\text{Au}(\text{C}\equiv\text{CCH}_2\text{OMe})\{\text{P}(p\text{-Tol})_3\}$  (149), and  $\{\text{Au}(\text{C}\equiv\text{CPh})\}_2(\mu\text{-PPri}_2\text{-4,4'-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-PPri}_2)$  (151) possess M-C bond lengths that differ from those of corresponding alkyl complexes by  $\Delta d(\text{M}-\text{C}) \cong 0.08$  Å (Table II). None of these alkynyl complexes possess unusually elongated  $\text{C}\equiv\text{C}$  bonds, consistent with the absence of structurally observable M-C  $\pi$ -bonding.



Unless one completely discounts the bond-ionicity arguments set out earlier, it appears that there are few instances where comparisons between metal-alkynyl and metal-alkyl M–C bond lengths provide unambiguous evidence for M–CCR  $\pi$ -bonding interactions, and thus interpreting structural data from such a standpoint is probably well grounded only if one has independent spectroscopic (or other) evidence for these interactions in the compounds under consideration.

## 2. Comparisons to Metal–Cyano Complexes

As pointed out in Section II, the electronic structures of analogous metal–cyano and metal–alkynyl complexes are viewed as being either quite similar or distinctly different, depending on the specific complexes under consideration and the experimental method used to probe their bonding. The possibility that differences between the natures of the M–CN and M–CCR bonds might be manifested in the molecular structures of these complexes makes comparisons of their M–C bond lengths of interest. The nominal single-bond covalent radius of both ligands is 0.69 Å, based on the C–C bond lengths of HC $\equiv$ C–C $\equiv$ CH [1.384(2) Å] and N $\equiv$ C–C $\equiv$ N [1.391(1) Å] (178), suggesting that, all other factors being equal, the M–C bond lengths of pairs of these complexes should be nearly identical. A first-order prediction of the relative M–C bond lengths of these complexes, however, would be  $d(\text{M–CN}) < d(\text{M–CCR})$ , for two reasons: First, the electronegativities of the two ligands differ significantly ( $\chi[\text{CN}] = 3.32$ ,  $\chi[\text{CCR}] = 2.4\text{--}2.8$ ) (160,166), which, based on the arguments outlined in the preceding section, should lead to a contraction of the M–CN bond length in complexes for which  $\chi[\text{ML}_n] < \chi[\text{CCR}] < \chi[\text{CN}]$ ; and second, the available evidence points to CN being a stronger  $\pi$ -acceptor than alkynyl ligands, which should shorten the M–CN bonds of complexes in which there are metal  $d\pi$ -electrons of appropriate energy for backbonding. (Conversely, alkynyl ligands should be better  $\pi$ -donors, on electronegativity grounds, which might favor shorter M–CCR bonds for high-valent complexes.)

The M–C bond lengths for pairs of analogous metal–alkynyl and metal–cyano complexes are set out in Table III (179–181). Interestingly, the first-order prediction for these bond lengths is not borne out; the lengths of the M–C bonds for the pairs of complexes VCp<sub>2</sub>R', *trans*-PtR'<sub>2</sub>(PR''<sub>3</sub>)<sub>2</sub> (182), and AuR'(PR''<sub>3</sub>) (R' = CN, CCR) are statistically indistinguishable from one another. The only complexes for which significant differences in M–C bond lengths are observed are those of the *trans*-WR'(≡CH)(dmpe)<sub>2</sub> class (16a–c). Interestingly, the W–CN bond is significantly *longer* than the W–CCR bonds of the alkynyl complexes. Spec-

TABLE III  
METAL–CARBON BOND LENGTHS FOR ANALOGOUS METAL–CYANO AND METAL–ALKYNYL COMPLEXES

Metal–cyano complex	$d(\text{M–C})$ (Å)	Ref.	Metal–alkynyl complex	$d(\text{M–C})$ (Å)	Ref.	$\Delta d^a$ (Å)
$\text{VCp}_2^*(\text{C}\equiv\text{N})$	2.088(7)	(179)	$\text{VCp}_2(\text{C}\equiv\text{CBu}')$	2.075(5)	(38)	0.01
$\text{trans-W}(\text{C}\equiv\text{N})(\text{CH})(\text{dmpe})_2$	2.292(4)	(16c)	$\text{trans-W}(\text{C}\equiv\text{CH})(\text{CH})(\text{dmpe})_2$	2.263(5)	(16c)	0.03
			$\text{trans-W}(\text{C}\equiv\text{CPh})(\text{CH})(\text{dmpe})_2$	2.250(4)	(16c)	0.04
			$\text{trans-W}(\text{C}\equiv\text{CSiMe}_3)(\text{CH})(\text{dmpe})_2$	2.246(6)	(16b)	0.05
			$\text{trans-W}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-CCPr}^a)(\text{CH})(\text{dmpe})_2$	2.245(8)	(16c)	0.05
$\text{trans-Pt}(\text{C}\equiv\text{N})_2(\text{PPh}_3)_2$	1.991(4)	(180)	$\text{trans-Pt}(\text{C}\equiv\text{CCPh})_2(\text{PMe}_2\text{Ph})_2$	2.009(5)	(5b,e)	−0.02
			$\text{trans-Pt}(\text{C}\equiv\text{CCMe}=\text{CH}_2)_2(\text{PPh}_3)_2$	2.024(6)	(108)	−0.03
$\text{Au}(\text{C}\equiv\text{N})(\text{PPh}_3)$	2.003(7)	(181)	$\text{Au}(\text{C}\equiv\text{CCH}_2\text{OMe})\{\text{P}(p\text{-Tol})_3\}$	2.024(2)	(149)	−0.02
			$\{\text{Au}(\text{C}\equiv\text{CPh})\}_2(\mu\text{-PPr}_2^i\text{-4,4'-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{PPr}_2^i)$	1.997(9)	(151)	0.01

<sup>a</sup>  $\Delta d = [d(\text{M–CN}) - d(\text{M–CCR})]$ .

troscopic and theoretical studies aimed at explaining this observation are in progress in our laboratory.

### 3. Influence of Alkynyl R-Group on M–C Distance

Metal complexes with alkynyl R-groups that are strongly electron donating or withdrawing might possess M–C bond lengths that differ from those for complexes whose alkynyl ligands lack these characteristics. One compound where such an effect might be operative,  $\text{CoCp}(\text{C}\equiv\text{C}-\text{C}\equiv\text{N})_2(\text{PPh}_3)$  (84), was discussed in Section III-C-1. Two other studies are of note in this regard. Carty and co-workers have reported high-quality structural data for complexes of the type *trans*- $\text{Ru}(\text{C}\equiv\text{CR})_2(\text{CO})_2(\text{PEt}_3)_2$  ( $\text{R} = \text{H}, \text{Ph}, \text{SiMe}_3, \text{C}\equiv\text{CH}, \text{C}\equiv\text{CSiMe}_3$ ) (63*a,b*). As noted in Section III-B, the  $\text{C}\equiv\text{C}$  bond lengths of *trans*- $\text{Ru}(\text{C}\equiv\text{CSiMe}_3)_2(\text{CO})_2(\text{PEt}_3)_2$  [1.221(2) Å] and *trans*- $\text{Ru}(\text{C}\equiv\text{CCCSiMe}_3)_2(\text{CO})_2(\text{PEt}_3)_2$  [1.226(2) Å] are unusually long, suggesting greater  $\text{Ru} \rightarrow \text{CCR}$   $\pi$ -backbonding for these species than for the other derivatives. Consistent with this, the Ru–C bond lengths of the former compounds [ $\text{R} = \text{SiMe}_3$ , 2.062(2) Å;  $\text{R} = \text{C}\equiv\text{CSiMe}_3$ , 2.057(2) Å] are significantly shorter than those of the ethynyl [2.078(1) Å], phenylethynyl [2.074(3) Å], and butadiynyl [2.078(2) Å] complexes. This ordering of Ru–C bond lengths would not be expected on electronegativity grounds (Section III-C-1). Unfortunately, a  $\text{Ru}-\text{C}_{sp^3}$  distance for an alkyl derivative of the type *trans*- $\text{RuR}'_2(\text{CO})_2(\text{PR}'')_2$  is not available for comparison.

Alkynyl-phosphorane ligands ( $\text{C}\equiv\text{CPR}_3$ ), such as those of the complexes  $\text{Mn}(\text{C}\equiv\text{CPh}_3)\text{Br}(\text{CO})_4$  (47),  $\text{MnCp}(\text{C}\equiv\text{CPMe}_2\text{Ph})(\text{CO})_2$  (48), and *cis*- $\text{Pd}(\text{C}\equiv\text{CPh}_3)(\text{PPh}_3)\text{Cl}_2$  (105), potentially support the limiting canonical structures  $\text{M}-\text{C}\equiv\text{C}-\text{PR}_3$  and  $\text{M}=\text{C}=\text{C}=\text{PR}_3$ . Moreover, they are unique among alkynyl ligands from a formal charge standpoint in that they are neutral rather than anionic. While this obviates comparisons of their M–C bond lengths to those of metal-alkyl, -cyano, and even other alkynyl complexes, it does present the only case where straightforward comparisons between alkynyl and carbon monoxide complexes can be made. For the pair of compounds  $\text{MnCp}(\text{C}\equiv\text{CPMe}_2\text{Ph})(\text{CO})_2$  and  $\text{MnCp}(\text{CO})_3$ , the Mn–CCR bond length [1.895(5) Å] (48) is observed to be 0.1 Å longer than those of the Mn–CO bonds of the latter compound [1.793(3) Å] (183). In contrast, the Mn–CO bond lengths of  $\text{MnCp}(\text{C}\equiv\text{CPMe}_2\text{Ph})(\text{CO})_2$  [1.743(7) Å] are 0.05 Å shorter than those of  $\text{MnCp}(\text{CO})_3$ . These data clearly indicate that the Mn–CCPR<sub>3</sub> bond order is lower than the Mn–CO bond order, and that the electron density available at the  $[\text{MnCp}(\text{CO})_2]$  fragment for  $\text{Mn} \rightarrow \text{CO}$   $\pi$ -backbonding is greater for the alkynyl complex than for  $\text{MnCp}(\text{CO})_3$ , suggesting that the alkynyl

ligand is a poorer  $\pi$ -acceptor and/or a better  $\sigma$ -donor than CO. Additional insight into the multiplicity of the Mn–C bond order for  $\text{MnCp}(\text{C}\equiv\text{CPh})(\text{CO})_2$  can be gleaned from the bond lengths of the Mn–C–P linkages within the ligand. Reference to the Cambridge Structural Database indicates that organic compounds of type  $\text{R}'_2\text{C}=\text{C}=\text{PR}_3$  (three structures reported) possess mean C=C and P=C bond lengths of 1.268(40) Å and 1.687(14) Å, respectively. By comparison,  $d(\text{C}=\text{CP}) = 1.221(7)$  Å and  $d(\text{CC}=\text{P}) = 1.683(6)$  Å for  $\text{MnCp}(\text{C}\equiv\text{CPh})(\text{CO})_2$  (48), suggesting that the  $\text{Mn}=\text{C}=\text{C}=\text{PR}_3$  canonical structure is a significant contributor to the bonding in this complex.

#### 4. Comparisons among Metal-Alkynyl Redox Congeners

A potentially important probe of the bonding in alkynyl complexes, and, in particular, the extent of  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding, is to determine how the  $\text{M}-\text{C}\equiv\text{C}-\text{R}$  fragment is structurally perturbed by the oxidation or reduction of the complex. The  $\text{M}-\text{C}\equiv\text{O}$  bond lengths of metal-carbonyl complexes are extremely sensitive to oxidation state, with M–C bonds lengthening and C≡O bonds contracting as the oxidation state of the metal increases (and, concomitantly,  $\text{M} \rightarrow \text{CO}$   $\pi$ -backbonding decreases) (154).

To date, there have been only two studies of this type for metal-alkynyl complexes. Whiteley and co-workers have reported the structures of the 18- and 17-electron complexes  $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CPh})(\text{dppe})]^{n+}$  ( $n = 0, 1$ ) (33g,42). Unlike the observation for metal-carbonyl complexes, the Mo–CCPh bond distance of the cation [2.067(9) Å] is 0.07 Å shorter than that of the neutral complex [2.138(5) Å]. This contraction of the M–C bond contrasts with the behavior of the Mo–P bonds of these redox partners, which lengthen by 0.06 Å upon oxidation. The C≡C bond distances of the neutral and cationic complexes are statistically indistinguishable, being 1.205(6) and 1.196(11) Å, respectively, as are the distances from the metal center to the centroid of the cycloheptatrienyl ligand (ca. 1.62 Å). The elongation of the Mo–P bonds upon oxidation was interpreted as reflecting lessened  $\text{Mo} \rightarrow \text{P}$   $\pi$ -backbonding in the oxidized compound, whereas the contraction of the Mo–C bond upon oxidation was said to be consistent with the smaller radius of  $\text{Mo}^{\text{I}}$  relative to that of  $\text{Mo}^0$  and the larger electrostatic contribution to the  $\text{Mo}^{\text{I}}-\text{C}$  bond as compared to the  $\text{Mo}^0-\text{C}$  bond. Thus,  $\text{Mo} \rightarrow \text{CCR}$   $\pi$ -backbonding appears to be of little or no importance to the bonding in these compounds. Infrared-spectroscopic data (Section IV-B) and electrochemical data were noted to support the conclusion that the Mo–CCR bond is predominantly of  $\sigma$ -character.

Bianchini and co-workers have prepared and structurally characterized redox congeners of the type  $[\text{Fe}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^{n+}$  ( $n = 0, 1$ ) (33a). As is observed for the Mo–P bonds of the  $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CPh})(\text{dppe})]^{n+}$  ( $n = 0, 1$ ) complexes from earlier, the Fe–P bonds of the cation are longer than those of the neutral complex [ $\Delta d$  (Fe–P) = 0.07–0.12 Å]. Unfortunately, the large esd's for the lengths of the Fe–C and C≡C bonds of these complexes [ $n = 0$ ,  $d(\text{Fe}-\text{C}) = 1.92(1)$  Å,  $d(\text{C}\equiv\text{C}) = 1.21(1)$  Å;  $n = 1$ ,  $d(\text{Fe}-\text{C}) = 1.88(2)$  Å,  $d(\text{C}\equiv\text{C}) = 1.20(3)$  Å] prohibit any quantitative differentiation of the natures of their Fe–CCR bonding. Infrared-spectroscopic data (Section IV-B) and electrochemical data for these compounds were interpreted as indicating that  $\text{Fe} \rightarrow \text{CCR} \pi$ -backbonding is insignificant.

#### D. C–R Bond Distances

The R-groups of alkynyl ligands that might be expected to exhibit variable C–R bond lengths as a function of the magnitude of M–CCR  $\pi$ -bonding include  $\text{PR}'_3$  and CN, since, as noted in Section III-C-3, canonical structures of the type  $\text{L}_n\text{M}=\text{C}=\text{C}=\text{R}$  can realistically be invoked for their complexes. The variable M–C and C≡C bond lengths of trimethylsilylethynyl complexes ( $\text{L}_n\text{M}-\text{C}\equiv\text{C}-\text{SiMe}_3$ ) suggest that C–Si bond lengths might also manifest a  $\pi$ -bonding component. In contrast, one can infer from these considerations that the C–R bond lengths of complexes of alkyl- and aryl-substituted alkynyl ligands should deviate little from the expectation values of their organic counterparts, and the data bear this out: The MCC–C(Ph) bond distances of phenylethynyl complexes, for which more precise data (22 distances with  $\text{esd} \leq 0.010$  Å) are available than for any other type of metal–alkynyl complex, span a range of only 0.041 Å [ $1.421(8)$ – $1.462(8)$  Å;  $d(\text{C}-\text{C})_{\text{mean}} = 1.439(9)$  Å], which is of marginal statistical significance and little different from the RCC–C(Ph) bond-length distribution for organic alkynes [ $d(\text{C}-\text{C})_{\text{mean}} = 1.435(9)$  Å for 55 distances with  $\text{esd} \leq 0.010$  Å].

The limited C–R bond-length data for  $\text{R} = \text{CN}$  and  $\text{R} = \text{PR}'_3$  alkynyl complexes have been noted earlier. For trimethylsilylethynyl complexes, the MCC–Si bond lengths span a range of 0.055 Å [ $1.797(7)$ – $1.852(8)$  Å, Table I;  $d(\text{C}-\text{Si})_{\text{mean}} = 1.819(22)$  Å], which, despite encompassing only nine distances ( $\text{esd} \leq 0.010$  Å), is broader than that for the MCC–C(Ph) distances of phenylethynyl complexes. Whether this is an indication that greater M–CCR  $\pi$ -bonding obtains for trimethylsilylethynyl complexes than for those in which the alkynyl R-group is an alkyl or aryl substituent is uncertain at this juncture, both because there is insufficient detailed

information about the electronic structures of these complexes to make any correlation to the  $d(\text{C-Si})$  distance, and because, among organic alkynes, the distribution of CC-Si bond lengths for silyl-substituted alkynes is also broader than that for alkyl- or aryl-substituted alkynes [1.809–1.864 Å,  $d(\text{C-Si})_{\text{mean}} = 1.834(14)$  Å for 14 distances with  $\text{esd} \leq 0.010$  Å]. The ambiguity concerning the interpretation of this bond length is well illustrated by the complex *trans*-Ru(C≡CSiMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> (63*b*). The short Ru-CC and long C≡C bonds of this compound have been noted earlier as being consistent with the presence of significant Ru → CCR  $\pi$ -backbonding, yet its CC-Si bond length [1.812(2) Å] is not significantly shorter than that of the mean distance for all trimethylsilylethynyl metal complexes. Despite these uncertainties, the CC-Si bond distance bears close examination in future studies, particularly in conjunction with <sup>29</sup>Si-NMR chemical shifts and MCC-Si nuclear spin-spin coupling constants, which have been reported to correlate with the extent of C-Si  $\pi$ -bonding (184), because of the preliminary indication that it is shorter for metal-alkynyl complexes than in organic alkynes.

#### E. The Structural *Trans* Influences of Alkynyl Ligands

An indirect measure of the nature of the metal-alkynyl bond is the *trans* influence exerted by the alkynyl ligand. There are several experimental parameters for assessing this influence, including structural (primarily bond length) and vibrational- and NMR-spectroscopic data for the ligand in question and for those oriented *trans* and *cis* to it (185). Well over a decade has passed since the *trans* influence of the alkynyl ligand has been a subject of detailed study, and several earlier papers provide leading references to this work and summarize the main conclusions (113, 116, 119, 186*a,b*). We will not review these older results, but instead provide an update on the structural *trans* influence of the alkynyl ligand in view of the wealth of recent crystallographic results. We note that the implications of the following observations for understanding the nature of metal-alkynyl bonding are not straightforward to set out because there is not a simple way experimentally to separate and individually quantify the factors that contribute to the structural *trans* influence of a ligand, such as its electronegativity and  $\sigma$ - and  $\pi$ -bonding character.

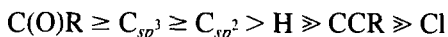
The original assessments of the *trans* influences of alkynyl ligands were made for square-planar Pt<sup>II</sup> complexes. Set out in Table IV (187–201) are crystallographically determined Pt-Cl bond lengths ( $\text{esd} \leq 0.006$  Å) for a variety of compounds of the type *trans*-Pt(X)Cl(PPh<sub>3-*n*</sub>R<sub>*n*</sub>)<sub>2</sub> ( $n = 0$  or 1), and the difference  $\Delta d(\text{Pt-Cl}) = [d(\text{XPt-Cl}) - d(\text{ClPt-Cl})]$  using

TABLE IV  
 STRUCTURAL DATA FOR *trans*-Pt(X)Cl(PR<sub>3</sub>)<sub>2</sub> COMPLEXES

PtCl(PR <sub>3</sub> ) <sub>2</sub>	X	<i>d</i> (Pt–Cl) (Å)	$\Delta d$ (Pt–Cl) <sup>a</sup> (Å)	Ref.
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)Pr <sup>n</sup>	2.450(4)	0.147	(187)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)CH <sub>2</sub> CH=CH <sub>2</sub>	2.439(5)	0.136	(188)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	Me	2.431(3)	0.128	(175)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)- <i>n</i> -C <sub>6</sub> H <sub>13</sub>	2.431(3)	0.128	(189)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)Me	2.430(2)	0.127	(190)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)CH <sub>2</sub> CH <sub>2</sub> Ph	2.427(6)	0.124	(191)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	2.425(2)	0.122	(192)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(O)C(O)Ph	2.421(3)	0.118	(193)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> -2-NMe <sub>2</sub>	2.416(3)	0.113	(194)
PtCl(PPh <sub>2</sub> Me) <sub>2</sub>	Me	2.412(2)	0.109	(195)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C(CMe=CH <sub>2</sub> )=CH <sub>2</sub>	2.410(3)	0.107	(119)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	Ph	2.408(5)	0.105	(196)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> Cl <sub>4</sub> -2-Au(PPh <sub>3</sub> )	2.406(2)	0.103	(197)
PtCl(PPh <sub>2</sub> Me) <sub>2</sub>	C(O)CF <sub>3</sub>	2.390(1)	0.087	(190)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> CN	2.390(3)	0.087	(198)
PtCl[P( <i>p</i> -Tol) <sub>3</sub> ] <sub>2</sub>	H	2.384(3)	0.081	(199)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C≡CCl	2.373(3)	0.070	(110)
PtCl(PPh <sub>2</sub> Me) <sub>2</sub>	C <sub>2</sub> F <sub>5</sub>	2.361(3)	0.058	(195)
		2.365(4)	0.062	
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C≡CCMe=CH <sub>2</sub>	2.363(6)	0.060	(112)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C≡CCMe <sub>2</sub> OH	2.356(5)	0.053	(113)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C≡C- <i>c</i> -C <sub>6</sub> H <sub>10</sub> -1-OEt	2.345(5)	0.042	(114)
PtCl(PPh <sub>3</sub> ) <sub>2</sub>	C≡CCMeEt(OH)	2.336(4)	0.033	(113)
PtCl[μ-dppf-W(CO) <sub>3</sub> ] <sub>2</sub>	Cl	2.304(5)	0.001	(200)
PtCl[PPh <sub>2</sub> CH <sub>2</sub> C(CF <sub>3</sub> ) <sub>2</sub> OH] <sub>2</sub>	Cl	2.303(1)	0	(201)

$$^a \Delta d(\text{Pt}–\text{Cl}) = [d(\text{XPt}–\text{Cl}) - d(\text{ClPt}–\text{Cl})].$$

*d*(Pt–Cl) for *trans*-PtCl<sub>2</sub>{PPh<sub>2</sub>CH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>(OH)}<sub>2</sub> as a reference. For acyl, alkyl, and aryl derivatives of *trans*-Pt(X)Cl(PPh<sub>3-*n*</sub>R<sub>*n*</sub>)<sub>2</sub>, the data reveal a near continuum of Pt–Cl bond lengths over the range  $\Delta d(\text{Pt}–\text{Cl}) = 0.10\text{--}0.15$  Å. The incorporation of strong electron withdrawing groups into these ligands [i.e., X = C(O)CF<sub>3</sub>, CH<sub>2</sub>CN, C<sub>2</sub>F<sub>5</sub>] lessens their *trans* influence, as indicated by the significantly shorter Pt–Cl bonds of their complexes ( $\Delta d = 0.06\text{--}0.09$  Å). The Pt–Cl bond lengths of alkynyl complexes are distinctly shorter than those *trans* to other carbon-ligated groups [ $\Delta d(\text{Pt}–\text{Cl}) = 0.03\text{--}0.07$  Å], indicating they have smaller *trans* influences. The differences among the Pt–Cl bond lengths of the alkynyl derivatives are of marginal statistical significance, so it is not possible to differentiate among their *trans* influences on the basis of these data. Overall, the *trans* influences of the X ligands can be ordered as follows:



This order is consistent with that derived in earlier studies (113,116, 119,186).

An important issue regarding the generality of these findings is the extent to which the *trans* influence of a ligand is dependent on the nature of the ligand *trans* to it, and on the nature of the metal. There are few other appropriate classes of structurally characterized metal-alkynyl complexes with which to address this question. Comparisons among the Au-P bond lengths ( $\text{esd} \leq 0.006 \text{ \AA}$ ) of complexes of the type  $\text{AuX}(\text{PPh}_3)$  (Table V) (202–205) reveal a similar ordering to that provided by the *trans*- $\text{Pt}(\text{X})\text{Cl}(\text{PR}_3)_2$  compounds. Moreover, the difference  $\Delta d(\text{Au-P}) = [d(\text{XAu-P}) - d(\text{ClAu-P})]$  [as determined relative to the Au-P bond length of  $\text{AuCl}(\text{PPh}_3)$ ] for alkynyl ligands is 0.04–0.05  $\text{\AA}$ , which is similar to the values of  $\Delta d(\text{Pt-Cl})$  for these ligands noted earlier (0.03–0.07  $\text{\AA}$ ). However, the difference between the *trans* influences of alkyl and alkynyl ligands, as judged by  $\Delta d(\text{Au-P})$ , is much smaller than that manifested by the Pt-Cl bond lengths of *trans*- $\text{Pt}(\text{X})\text{Cl}(\text{PR}_3)_2$  complexes of these ligands. The  $\text{AuX}(\text{PPh}_3)$  compounds also provide comparisons of the cyanide and alkynyl ligands; the similar Au-P bond lengths for these compounds suggest that their *trans* influences are essentially identical (Table V).

The only relevant data for other than late-metal alkynyl complexes are provided *trans*- $\text{FeCl}_2(\text{dmpe})_2$  [ $d(\text{Fe-Cl}) = 2.352(1) \text{ \AA}$ ] (206), *trans*- $\text{Fe}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dmpe})_2$ , for which two independent crystal structures have

TABLE V  
GOLD-PHOSPHORUS BOND DISTANCES FOR  $\text{AuX}(\text{PPh}_3)$  COMPLEXES

X	$d(\text{Au-P})$ ( $\text{\AA}$ )	$\Delta d(\text{Au-P})^a$ ( $\text{\AA}$ )	Ref.
$\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Ph}$	2.292(3)	0.057	(176)
$\text{CH}_2\text{C}(\text{O})\text{Ph}$	2.283(1)	0.049	(176)
$\text{C}_6\text{H}_5\text{-2,6-(OMe)}_2$	2.284(1)	0.048	(202)
$\text{C}\equiv\text{CPh}$	2.282(4)	0.047	(146)
	2.276(5)	0.041	
$\text{C}\equiv\text{N}$	2.278(2)	0.043	(181)
$\text{C}\equiv\text{CCH}_2\text{OMe}$	2.274(1) <sup>b</sup>	0.039	(149)
$\text{C}\equiv\text{CC}_6\text{F}_5$	2.274(3)	0.039	(148)
Br	2.252(6)	0.017	(203)
I	2.249(2)	0.014	(204)
Cl	2.235(3)	0	(205)

<sup>a</sup>  $\Delta d(\text{Au-P}) = [d(\text{XAu-P}) - d(\text{ClAu-P})]$ .

<sup>b</sup> Distance for  $\text{Au}(\text{C}\equiv\text{CCH}_2\text{OMe})\{\text{P}(p\text{-Tol})_3\}$ .



been reported [ $d(\text{Fe}-\text{Cl}) = 2.389(1) \text{ \AA}$  (53),  $2.386(2) \text{ \AA}$  (54);  $d(\text{Fe}-\text{C}) = 1.897(3) \text{ \AA}$  (53),  $1.880(5) \text{ \AA}$  (54)] and *trans*- $\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{dmpe})_2$  [ $d(\text{Fe}-\text{C}) = 1.925(6) \text{ \AA}$ ] (52*a,b*). The facts that the Fe-Cl bond of the mono(phenylethynyl) derivative is ca.  $0.035 \text{ \AA}$  longer than those of the dichloro complex, and that its Fe-C bond is ca.  $0.03 \text{ \AA}$  shorter than those of the bis(phenylethynyl) compound, are consistent with the findings for *trans*- $\text{Pt}(\text{X})\text{Cl}(\text{PR}_3)_2$  and  $\text{AuX}(\text{PPh}_3)$  in indicating the *trans* influence of alkynyl ligands to be significantly greater than that of chloride.

## IV

### VIBRATIONAL SPECTROSCOPIC STUDIES

#### A. Overview

The considerations set out in Section III that justify inspecting the M-C,  $\text{C}\equiv\text{C}$ , and C-R bond distances of metal-alkynyl complexes for insight into the nature of the M-CCR bond also apply to the respective stretching frequencies of these linkages. Compared to the study of bond distances, there are several potential advantages to using vibrational frequencies in this regard, including their greater precision and sensitivity to electronic effects and the relative ease with which the experiments are performed. Consider, for example, the  $\text{C}\equiv\text{C}$  bond distances and stretching frequencies of metal-alkynyl complexes. The 150 or so X-ray crystallographic studies of metal-alkynyl compounds have yielded roughly 50 structures with precise  $\text{C}\equiv\text{C}$  bond distances; these distances span only a  $0.10\text{-}\text{\AA}$  range, with two-thirds of them lying in a  $0.025\text{-}\text{\AA}$  range (Fig. 2). In contrast,  $\text{C}\equiv\text{C}$  stretching frequencies are known for the majority of all metal-alkynyl complexes; more than 350 such frequencies have been reported for phenylethynyl complexes alone, and they cover a range of nearly  $180 \text{ cm}^{-1}$  (*vide infra*).

Of course, in order to use vibrational spectroscopy to study metal-alkynyl bonding the vibrational modes of interest must be assigned. This is fairly easy for  $\nu(\text{C}\equiv\text{C})$  because of its distinctive frequency range, but, with few exceptions, is difficult for  $\nu(\text{M}-\text{C})$  and  $\nu(\text{C}-\text{R})$  because bands attributable to the ancillary ligands and alkynyl R-groups congest these frequency regions. Unfortunately, there are insufficient M-C and C-R stretching-frequency data to warrant detailed discussions of their significance regarding the nature of metal-alkynyl bonding. While the frequency of the  $\nu(\text{C}-\text{R})$  mode is not expected to be an especially sensitive reporter

of the nature of M-CCR bonding, the paucity of  $\nu(\text{M}-\text{C})$  frequency data is a significant loss in this regard; a detailed study of these modes for complexes whose synthetic accessibility and symmetry allowed both isotopic labeling of the alkynyl ligand and a normal-coordinate analysis would be an important addition to the field.

### B. $\text{C}\equiv\text{C}$ Stretching Frequencies

The long-standing use of  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{N}$  stretching frequencies to gauge qualitatively the extent of  $\text{M} \rightarrow \text{CO}$  and  $\text{M} \rightarrow \text{CN}$   $\pi$ -backbonding in metal-carbonyl and -cyano complexes has naturally led to  $\text{C}\equiv\text{C}$  stretching frequencies of metal-alkynyl complexes being interpreted within the framework of  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding. The alkynyl R-group complicates the interpretation of  $\text{C}\equiv\text{C}$  stretching frequencies, as compared to those of the  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{N}$  oscillators, because of the possibility that the nominal  $\nu(\text{C}\equiv\text{C})$  mode might consist not of just the  $\text{C}\equiv\text{C}$  stretch but of C-R and R-group symmetry coordinates as well (207). This is well established for terminal alkynes, for which both the  $\text{C}\equiv\text{C}$  and the terminal C-H stretching coordinates contribute to " $\nu(\text{C}\equiv\text{C})$ ." Clearly, the safest approach to interpreting  $\text{C}\equiv\text{C}$  stretching frequencies is to limit comparisons among them to within groups of complexes that share a common alkynyl R-group.

As was discussed for the  $\text{C}\equiv\text{C}$  bond distance (Section III-B), a good way to approach the interpretation of the  $\text{C}\equiv\text{C}$  stretching frequencies of metal-alkynyl complexes is to examine their distribution. Although frequency data for metal-alkynyl complexes are abundant, they are divided among compounds with many different alkynyl R-groups. There are too few data for complexes of most alkynyl ligands to provide distributions within which trends can be discussed in a statistically significant way; unfortunately, this includes complexes with electron-withdrawing alkynyl R-groups, for which  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding (and hence  $\nu(\text{C}\equiv\text{C})$  frequency shifts) should be greatest. Complexes of the phenylethynyl ligand are the major exception to this, since over 350  $\text{C}\equiv\text{C}$  stretching frequencies have been reported for them; Table VI (208-336) sets out these data. The frequencies therein are those specifically assigned by the reporting authors as being attributable to  $\nu(\text{C}\equiv\text{C})$ ; we have not included frequencies for compounds for which the vibrational data are given as unassigned listings, even when these contained "obvious" candidates for  $\nu(\text{C}\equiv\text{C})$ , or for which the frequency is referred to as being "approximate." We note the experimental conditions under which the spectra were acquired, although solvent and medium effects appear to be of minor importance in the few

TABLE VI  
C≡C STRETCHING FREQUENCIES FOR METAL-PHENYLETHYNYL COMPLEXES

Compound	$\nu(\text{C}\equiv\text{C})^a$ (cm <sup>-1</sup> )	Ref.
TiCp <sub>2</sub> (C≡CPh) <sub>2</sub>	2070 <sup>c</sup>	(208a,b)
	2065 <sup>b</sup>	(209a,b)
Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (C≡CPh) <sub>2</sub>	2045 <sup>b</sup>	(209a,b)
Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> (C≡CPh) <sub>2</sub>	2066 <sup>c</sup>	(209b)
Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me)(C≡CPh)(NMe <sub>2</sub> ) <sub>2</sub>	2080 <sup>b</sup>	(210)
ZrCp <sub>2</sub> (C≡CPh) <sub>2</sub>	2075 <sup>c</sup>	(35)
	2073 <sup>b</sup>	(210)
Zr(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (C≡CPh) <sub>2</sub>	2070 <sup>c</sup>	(35)
	2078 <sup>b</sup>	(210)
Zr(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> (C≡CPh) <sub>2</sub>	2078 <sup>c</sup>	(35)
ZrCp <sub>2</sub> (C≡CPh)Cl	2074 <sup>c</sup>	(35)
Zr(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (C≡CPh)Cl	2070 <sup>c</sup>	(35)
HfCp <sub>2</sub> (C≡CPh) <sub>2</sub>	2080 <sup>c</sup>	(35)
	2083 <sup>b</sup>	(210,211) <sup>c</sup>
Hf(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>2</sub> (C≡CPh) <sub>2</sub>	2072 <sup>c</sup>	(212)
VCp <sub>2</sub> (C≡CPh)	2060 <sup>c</sup>	(208a)
VCp <sub>2</sub> (C≡CPh) <sub>2</sub>	2060 <sup>c</sup>	(208a)
V(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> Et) <sub>2</sub> (C≡CPh)	2040 <sup>d</sup>	(31b)
[N(PPh <sub>3</sub> ) <sub>2</sub> ][Cr(C≡CPh)(CO) <sub>3</sub> ]	2080 <sup>c</sup>	(213)
K <sub>3</sub> [Cr(C≡CPh) <sub>3</sub> (CO) <sub>3</sub> ]	2176 <sup>c</sup>	(214)
Li[CrPc(C≡CPh) <sub>2</sub> ]	2065, 2075	(215)
CrCp(C≡CPh)(CO) <sub>3</sub>	2110 <sup>c</sup>	(216)
[N(PPh <sub>3</sub> ) <sub>2</sub> ][Mo(C≡CPh)(CO) <sub>5</sub> ]	2079 <sup>c</sup>	(213)
[N(PPh <sub>3</sub> ) <sub>2</sub> ][Mo(C≡CPh)(CO) <sub>4</sub> (PPh <sub>3</sub> )]	2058 <sup>c</sup>	(213)
K <sub>3</sub> [Mo(C≡CPh) <sub>3</sub> (CO) <sub>3</sub> ]	2190 <sup>c</sup>	(217)
<i>trans</i> -Mo(C≡CPh) <sub>2</sub> (dppe) <sub>2</sub>	2020 <sup>c</sup>	(33f)
Mo(C≡CPh) <sub>2</sub> H <sub>2</sub> (depe) <sub>2</sub>	2040 <sup>c</sup>	(33f)
MoCp(C≡CPh)(CO) <sub>3</sub>	2110 <sup>b</sup>	(218)
	2100 <sup>b</sup>	(219)
MoCp <sub>2</sub> (C≡CPh) <sub>2</sub>	2090	(220)
Mo(η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> )(C≡CPh)(CO) <sub>2</sub>	2078 <sup>c</sup>	(33n)
Mo(η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> )(C≡CPh)(dppe)	2045 <sup>c</sup>	(33n)
[Mo(η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> )(C≡CPh)(dppe)][BF <sub>4</sub> ]	2032 <sup>c</sup>	(33n)
[N(PPh <sub>3</sub> ) <sub>2</sub> ][W(C≡CPh)(CO) <sub>3</sub> ]	2080 <sup>c</sup>	(213)
[N(PPh <sub>3</sub> ) <sub>2</sub> ][W(C≡CPh)(CO) <sub>4</sub> (PPh <sub>3</sub> )]	2065 <sup>c</sup>	(213)
Li[ <i>fac</i> -W(C≡CPh)(dppe)(CO) <sub>3</sub> ]	2030 <sup>k</sup>	(221)
<i>trans</i> -W(C≡CPh) <sub>2</sub> (dppe) <sub>2</sub>	2040 <sup>c</sup>	(33f)
W(C≡CPh) <sub>2</sub> H <sub>2</sub> (dppe) <sub>2</sub>	2040 <sup>c</sup>	(33f)
<i>trans</i> -W(C≡CPh)(CH)(dmpe) <sub>2</sub>	2060	(16c)
WCp(C≡CPh)(CO) <sub>3</sub>	2105 <sup>c</sup>	(222)
	2110 <sup>b</sup>	(218)
	2110 <sup>c</sup>	(216)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\text{WCp}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PMe}_3)$	2082 <sup>c</sup>	(223)
$\text{WCp}_2(\text{C}\equiv\text{CPh})_2$	2080	(220)
$\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CPh})(\text{CO})_2$	2080 <sup>e</sup>	(33 <i>n</i> )
$\text{WTP}'(\text{C}\equiv\text{CPh})(\text{HCCPh})(\text{CO})$	2070 <sup>c</sup>	(224)
$\text{Ba}[\text{Mn}(\text{C}\equiv\text{CPh})_4]$	2048	(225)
$\text{Mn}(\text{C}\equiv\text{CPh})(\text{CO})_5$	2120 <sup>f</sup>	(226)
$\text{Mn}(\text{C}\equiv\text{CPh})(\text{CO})(\text{dppe})_2$	2056 <sup>e</sup>	(227 <i>a, b</i> )
<i>cis</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{PCy}_3)(\text{CO})_4$	2106 <sup>e</sup>	(227 <i>a</i> )
	2111 <sup>g</sup>	(227 <i>b</i> )
<i>trans, mer</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{PEt}_3)_2(\text{CO})_3$	2092 <sup>e</sup>	(227 <i>b</i> )
<i>trans, mer</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{PCy}_3)_2(\text{CO})_3$	2093 <sup>e</sup>	(227 <i>a, b</i> )
<i>cis</i> - $\text{Mn}(\text{C}\equiv\text{CPh})\{\text{P}(\text{OMe})_3\}(\text{CO})_2(\text{dppe})$	2084 <sup>e</sup>	(227 <i>b</i> )
<i>cis</i> - $\text{Mn}(\text{C}\equiv\text{CPh})\{\text{P}(\text{OEt})_3\}(\text{CO})_2(\text{dppe})$	2084 <sup>e</sup>	(227 <i>b</i> )
<i>cis</i> - $\text{Mn}(\text{C}\equiv\text{CPh})\{\text{P}(\text{OPh})_3\}(\text{CO})_2(\text{dppe})$	2093 <sup>e</sup>	(227 <i>b</i> )
<i>cis</i> - $\text{Mn}(\text{C}\equiv\text{CPh})\{\text{P}(\text{OPh})_3\}(\text{CO})_2(\text{dppm})$	2089 <sup>e</sup>	(227 <i>b</i> )
<i>fac</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{dppm})(\text{CO})_3$	2099 <sup>e</sup>	(227 <i>b</i> )
<i>fac</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{dppe})(\text{CO})_3$	2097 <sup>e</sup>	(227 <i>a, b</i> )
<i>fac</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{phen})(\text{CO})_3$	2089 <sup>e</sup>	(227 <i>b</i> )
<i>fac</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{bpy})(\text{CO})_3$	2094 <sup>e</sup>	(227 <i>b</i> )
<i>fac</i> - $\text{Mn}(\text{C}\equiv\text{CPh})(\text{CNBu}'(\text{PCy}_3)(\text{CO})_3$	2093 <sup>e</sup>	(227 <i>b</i> )
$\text{Re}(\text{C}\equiv\text{CPh})(\text{CO})_5$	2120 <sup>f</sup>	(226)
	2112 <sup>f</sup>	(228)
<i>fac</i> - $\text{Re}(\text{C}\equiv\text{CPh})(\text{py})_2(\text{CO})_3$	2090 <sup>b</sup>	(49)
$\text{Re}(\text{C}\equiv\text{CPh})\text{Cl}\{\text{P}(\text{O})(\text{OMe})_2\}\{\text{P}(\text{OMe})_3\}_2(\text{PPh}_3)$	2015 <sup>c</sup>	(229)
$\text{Re}(\text{C}\equiv\text{CPh})\text{Cl}\{\text{P}(\text{O})(\text{OMe})_2\}\{\text{P}(\text{OMe})_3\}(\text{NCMe})_2$	2040 <sup>c</sup>	(229)
$\text{ReCp}(\text{C}\equiv\text{CPh})(\text{NO})(\text{PPh}_3)$	2082 <sup>h</sup>	(50)
$\text{Re}_2(\text{C}\equiv\text{CPh})(\text{CO})_7(\mu\text{-dppm})(\mu\text{-H})$	2098 <sup>i</sup>	(51)
<i>trans</i> - $\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{dmpe})_2$	2037	(52 <i>a, b</i> )
<i>trans</i> - $\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{depe})_2$	2046 <sup>j</sup>	(230)
	2035	(52 <i>a</i> )
	2038 <sup>c</sup>	(61)
$\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{dbpe})_2$	2038	(231)
<i>trans</i> - $\text{Fe}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dmpe})_2$	2044	(52 <i>a, 53b</i> ) <sup>b</sup>
<i>trans</i> - $\text{Fe}(\text{C}\equiv\text{CPh})(\text{H})(\text{dmpe})_2$	2036 <sup>j</sup>	(232)
$\text{Fe}(\text{C}\equiv\text{CPh})(\text{H})(\text{dmpe})_2$	2035 <sup>c</sup>	(233)
$[\text{PPh}_4]_2[\text{Fe}(\text{C}\equiv\text{CPh})(\text{CN})_4(\text{NO})]$	2097	(234)
$[\text{PPh}_4]_2[\text{fac-Fe}(\text{C}\equiv\text{CPh})_3(\text{CN})_2(\text{NO})]$	2056	(234)
$\text{Fe}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}$	2030	(33 <i>a</i> )
$[\text{Fe}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$	2035	(235)
$\text{FePc}(\text{C}\equiv\text{CPh})$	2080 <sup>c</sup>	(215)
$\text{Li}_2[\text{FePc}(\text{C}\equiv\text{CPh})_2]$	2080 <sup>c</sup>	(236)
	2066, 2076	(237)
$\text{Na}[\text{FePc}(\text{C}\equiv\text{CPh})]$	2084 or 2112	(238)

(continued)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\text{E}[\text{FePc}(\text{C}\equiv\text{CPh})(\text{py})]$		
E = Li	2088	(237)
E = Na	2036 or 2082	(238)
$\text{FeCp}(\text{C}\equiv\text{CPh})(\text{CO})_2$	2105 <sup>b</sup>	(219, 222)
	2104 <sup>c,e</sup>	(59)
	2108 <sup>e</sup>	(12b)
	2121 <sup>f</sup>	(228)
	2121 <sup>b</sup>	(218)
$\text{FeCp}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)$	2085 <sup>b</sup>	(219)
$\text{FeCp}(\text{C}\equiv\text{CPh})(\text{dppm})$	2071 <sup>c</sup>	(58)
$\text{FeCp}^*(\text{C}\equiv\text{CPh})(\text{CO})_2$	2094 <sup>c</sup>	(59)
	2095 <sup>e</sup>	(59)
$\text{FeCp}^*(\text{C}\equiv\text{CPh})(\text{dppe})$	2054 <sup>c</sup>	(33a)
$[\text{FeCp}^*(\text{C}\equiv\text{CPh})(\text{dppe})][\text{PF}_6]$	2022	(33d)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_4$	2070 <sup>c</sup>	(239)
	2055	(240)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{dppe})_2$	2061 <sup>e</sup>	(61)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{depe})_2$	2054 <sup>c</sup>	(61)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dppm})_2$	2075 <sup>b</sup>	(62a)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{CO})_2(\text{PEt}_3)_2$	2093 <sup>e</sup>	(63a)
<i>cis, cis, trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{CO})_2(\text{PPr}^i_3)_2$	2095 <sup>j</sup>	(241)
$\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{PPh}_3)_3$	2075 <sup>c</sup>	(242)
<i>trans, cis</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2(\text{CO})(\text{PPr}^i_3)$	2070 <sup>j</sup>	(241)
<i>trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PPr}^i_3)_2$	2090 <sup>j</sup>	(241)
$\text{Ru}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{PPr}^i_3)_2$	2060 <sup>j</sup>	(241, 243) <sup>b</sup>
$\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}(\text{pzH-3,5-Me}_2)(\text{CO})(\text{PPh}_3)_2$	2085 <sup>b</sup>	(244)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})(\text{PPh}_3)_3$	2012 <sup>c</sup>	(242)
<i>cis, trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})_2(\text{PPr}^i_3)_2$	2090 <sup>j</sup>	(241)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PPr}^i_3)_2$	2078 <sup>j</sup>	(241)
<i>cis, trans</i> - $\text{Ru}(\text{C}\equiv\text{CPh})(\text{CH}=\text{CHPh})(\text{CO})_2(\text{PPr}^i_3)_2$	2098 <sup>b</sup>	(243)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{CH}=\text{CHPh})(\text{CO})(\text{PPr}^i_3)_2$	2065 <sup>b</sup>	(243)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$	2090 <sup>c</sup>	(245)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{O}_2\text{CCH}_3)(\text{CO})(\text{PPh}_3)_2$	2100 <sup>c</sup>	(245)
$\text{Ru}(\text{C}\equiv\text{CPh})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2$	2120	(246)
<i>mer</i> - $\text{Ru}(\text{C}\equiv\text{CPh})(\eta^2\text{-H}_2\text{BH}_2)(\text{PMe}_3)_3$	2050 <sup>c</sup>	(247)
$[\text{cis, trans-Ru}(\text{C}\equiv\text{CPh})(\text{CO})(\text{py})_2(\text{PPh}_3)_2]\text{X}$	2100 <sup>c</sup>	(64)
X = $\text{BF}_4$ , $\text{ClO}_4$ , $\text{PF}_6$		
$[\text{cis, trans-Ru}(\text{C}\equiv\text{CPh})(\text{py})(\text{CO})_2(\text{PPh}_3)_2][\text{PF}_6]$	2110 <sup>c</sup>	(65)
$\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}\{\text{PPh}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2\}$	2060 <sup>c</sup>	(248)
$[\text{Ru}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$	2062	(249)
$\text{Ru}(\text{C}\equiv\text{CPh})(\eta^3\text{-PhC}\equiv\text{C}-\text{C}=\text{CHPh})\{\text{PPh}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2\}$	2060 <sup>c</sup>	(66b, 248)
$\text{Li}[\text{RuPc}(\text{C}\equiv\text{CPh})]$	2062	(236)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_2$	2105	(250)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$	2068	(251a, b)
	2076 <sup>i</sup>	(252)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{PMe}_3)(\text{PPh}_3)$	2070	(250)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\text{RuCp}(\text{C}\equiv\text{CPh})\{\text{P}(\text{OMe})_3\}_2$	2085	(253)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{dppe})$	2083	(254)
	2082	(251b)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{dppm})$	2080	(254)
	2077	(251b)
$\text{RuCp}(\text{C}\equiv\text{CPh})(\text{dppf})$	2112 <sup>c</sup>	(255)
$\text{RuCp}^*(\text{C}\equiv\text{CPh})(\text{dppe})$	2071 <sup>c</sup>	(33o)
$\text{Ru}_2\text{Cp}^*_2(\text{C}\equiv\text{CPh})_2(\mu\text{-SPri})_2$	2100 <sup>c</sup>	(75,256)
$\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{C}\equiv\text{CPh})(\text{PMe}_3)\text{Cl}$	2090	(257)
<i>trans</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{dppm})_2$	2069 <sup>e</sup>	(61)
<i>cis</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_4$	2050	(239)
$\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{PPri}^i)_2(\text{pzH})$	2070	(76)
$\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{PPri}^i)_2$	2060 <sup>i</sup>	(241,258)
	2060	(76)
<i>trans</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PPri}^i)_2$	2080 <sup>j</sup>	(241)
<i>trans</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{PMe}_3)(\text{PPri}^i)_2$	2090 <sup>j</sup>	(241)
<i>trans, cis</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2(\text{CO})(\text{PPri}^i)_2$	2070 <sup>i</sup>	(241)
<i>trans</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})_2(\text{PPri}^i)_2$	2090 <sup>j</sup>	(241)
<i>trans</i> - $\text{Os}(\text{C}\equiv\text{CPh})_2(\text{CO})(\text{HC}\equiv\text{CPh})(\text{PPri}^i)_2$	2090 <sup>j</sup>	(241)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})(\text{pzH})(\text{PPri}^i)_2$	2150	(76)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PPri}^i)_2$	2090	(76)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PMeBu}^i)_2$	2060 <sup>e</sup>	(241)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})_2(\text{PPri}^i)_2$	2095	(76)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})(\text{PPri}^i)_2$	2090 <sup>j</sup>	(76)
$\text{Os}(\text{C}\equiv\text{CPh})(\text{H})(\text{H}_2)(\text{CO})(\text{PPri}^i)_2$	2090 <sup>j</sup>	(76)
$\text{OsCp}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$	2066	(251b)
$\text{OsCp}(\text{C}\equiv\text{CPh})(\text{dppe})$	2090	(259)
$[\text{OsCp}^*(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)][\text{BF}_4]$	2095 <sup>e</sup>	(260)
$\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{C}\equiv\text{CPh})\text{I}(\text{PMe}_3)$	2095 <sup>e</sup>	(261)
$\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{C}\equiv\text{CPh})\text{I}(\text{PMe}_2\text{Bu}^i)$	2090 <sup>e</sup>	(261)
$\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{C}\equiv\text{CPh})\text{I}(\text{PMeBu}^i)_2$	2085 <sup>e</sup>	(261)
$\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{C}\equiv\text{CPh})\text{I}(\text{PPri}^i)_2$	2085 <sup>c</sup>	(262)
$\text{E}[\text{Q}]_3[\text{Co}(\text{C}\equiv\text{CPh})_6]$	2045	(263)
E = Na, K; Q = PPh <sub>4</sub> , AsPh <sub>4</sub>		
$\text{Na}_2[\text{Co}(\text{C}\equiv\text{CPh})_4(\text{PET}_3)_2]$	2044	(264)
$\text{Na}[\text{PPh}_4][\text{Co}(\text{C}\equiv\text{CPh})_4(\text{PPh}_3)_2]$	2050	(264)
$\text{Co}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_4$	2018	(265)
$\text{Co}(\text{C}\equiv\text{CPh})_2(\text{dppe})_2$	2068	(264)
	2064 <sup>j,m</sup>	
$[\text{trans-Co}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_4]\text{X}$		
X = BF <sub>4</sub>	2055	(83)
X = BPh <sub>4</sub>	2060	(83)
$[\text{trans-Co}(\text{C}\equiv\text{CPh})(\text{H})(\text{depe})_2][\text{BPh}_4]$	2096	(80)
<i>fac, cis</i> - $\text{Co}(\text{C}\equiv\text{CPh})_2(\text{H})(\text{PMe}_3)_3$	2068, 2080	(78)

(continued)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
<i>mer, cis</i> -Co(C $\equiv$ CPh) <sub>2</sub> (H)(PMe <sub>3</sub> ) <sub>3</sub>	2058, 2080	(78)
<i>mer, trans</i> -Co(C $\equiv$ CPh) <sub>2</sub> (H)(PMe <sub>3</sub> ) <sub>3</sub>	2058, 2080	(78)
	2080 <sup>i</sup>	
Co(C $\equiv$ CPh) <sub>2</sub> (H)(PMe <sub>3</sub> ) <sub>3</sub>	2055, 2077	(83)
	2080 <sup>i</sup>	
<i>mer</i> -Co(C $\equiv$ CPh)(H)(Ph)(PMe <sub>3</sub> ) <sub>3</sub>	2083	(78)
Co(C $\equiv$ CPh){P(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }	2050	(33j, 82)
[Co(C $\equiv$ CPh){P(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [BPh <sub>4</sub> ]	2070	(33j)
[Co(C $\equiv$ CPh)(H){P(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [BPh <sub>4</sub> ]	2085	(82)
CoPc(C $\equiv$ CPh)	2128 <sup>c</sup>	(215)
Li <sub>2</sub> [CoPc(C $\equiv$ CPh)] <sub>2</sub>	2096	(215)
Li[CoPc(C $\equiv$ CPh)] <sub>2</sub>	2092, 2103	(215)
Co(Salen)(C $\equiv$ CPh)(py)	2120 <sup>b</sup>	(266)
Co(Salen)(C $\equiv$ CPh)(N <sub>2</sub> C <sub>4</sub> H <sub>6</sub> )	2110 <sup>b</sup>	(267)
<i>trans</i> -Co{N <sub>4</sub> }(C $\equiv$ CPh) <sub>2</sub>	2113 <sup>b</sup>	(268)
<i>trans</i> -Co{N <sub>4</sub> }(C $\equiv$ CPh)Cl	2126 <sup>b</sup>	(268)
<i>trans</i> -Co{N <sub>4</sub> }(C $\equiv$ CPh)I	2120 <sup>c</sup>	(81)
[ <i>trans</i> -Co{N <sub>4</sub> }(C $\equiv$ CPh)(NC <sub>5</sub> H <sub>4</sub> -4-Bu <sup>t</sup> )] [PF <sub>6</sub> ]	2110 <sup>c</sup>	(81)
[NBu <sup>n</sup> <sub>4</sub> ][ <i>trans</i> -Rh(C $\equiv$ CPh)Cl(PPr <sup>i</sup> ) <sub>3</sub> ]	2030 <sup>k</sup>	(269)
Rh(C $\equiv$ CPh)(PMe <sub>3</sub> ) <sub>4</sub>	2081	(85)
Rh(C $\equiv$ CPh)(dmpe) <sub>2</sub>	2077 <sup>g</sup>	(85)
<i>trans</i> -Rh(C $\equiv$ CPh)(py)(PPr <sup>i</sup> ) <sub>3</sub>	2055 <sup>g</sup>	(270)
<i>trans</i> -Rh(C $\equiv$ CPh)(C <sub>2</sub> H <sub>4</sub> )(PPr <sup>i</sup> ) <sub>3</sub>	2060 <sup>j</sup>	(270)
<i>cis</i> -Rh(C $\equiv$ CPh)(PCy <sub>3</sub> )(cod)	2081	(271)
Rh(C $\equiv$ CPh)(PPh <sub>3</sub> ) <sub>3</sub>	2100	(272a, b)
Rh(C $\equiv$ CPh)(CO)(PCy <sub>3</sub> ) <sub>2</sub>	2090 <sup>e</sup>	(271)
Rh(C $\equiv$ CPh)(CO)(PPh <sub>3</sub> ) <sub>2</sub>	2092	(272a, b)
	2094	(222a, b)
<i>trans</i> -Rh(C $\equiv$ CPh)(C=CHPh)(PPr <sup>i</sup> ) <sub>3</sub>	2070 <sup>c</sup>	(273)
<i>trans, mer</i> -Rh(C $\equiv$ CPh) <sub>2</sub> (H)(PMe <sub>3</sub> ) <sub>3</sub>	2097 <sup>g</sup>	(90)
<i>trans, mer</i> -Rh(C $\equiv$ CPh) <sub>2</sub> (H)(PBu <sup>n</sup> ) <sub>3</sub>	2085 <sup>h</sup>	(86a)
Rh(C $\equiv$ CPh) <sub>2</sub> (SnMe <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2073, 2082	(272a, b)
<i>trans, mer</i> -Rh(C $\equiv$ CPh) <sub>2</sub> (SnMe <sub>3</sub> )(PMe <sub>3</sub> ) <sub>3</sub>	2093	(274)
Rh(C $\equiv$ CPh)(H)Cl(PPr <sup>i</sup> ) <sub>3</sub>	2105 <sup>j</sup>	(270)
Rh(C $\equiv$ CPh)(H)Cl(py)(PPr <sup>i</sup> ) <sub>3</sub>	2100 <sup>c</sup>	(270, 275)
Rh(C $\equiv$ CPh)Cl(OSO <sub>2</sub> CF <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	2144 <sup>b</sup>	(276)
Rh(C $\equiv$ CPh){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }	2080	(33m, 88a, b)
[Rh(C $\equiv$ CPh){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }]X	2115	(33h, m, 88b)
X = BF <sub>4</sub> , ClO <sub>4</sub> , PF <sub>6</sub> , BPh <sub>4</sub>		
[Rh(C $\equiv$ CPh){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [PF <sub>6</sub> ] <sub>2</sub>	2125	(33h)
[Rh(C $\equiv$ CPh){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }(EtOH)]X <sub>2</sub>	2125	(33h)
X = PF <sub>6</sub> , BF <sub>4</sub>		
[Rh(C $\equiv$ CPh){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }(OCMe <sub>2</sub> )] [PF <sub>6</sub> ] <sub>2</sub>	2125	(33h)
[Rh(C $\equiv$ CPh)(H){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }]X	2120	(88a, 277)
X = BPh <sub>4</sub> , SO <sub>3</sub> CF <sub>3</sub>		
[Rh(C $\equiv$ CPh)(O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -3-Cl){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [BPh <sub>4</sub> ]	2120	(278)
[Rh(C $\equiv$ CPh)(OH){N(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }] [BPh <sub>4</sub> ]	2115	(278)
Rh(C $\equiv$ CPh){P(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }	2070	(88a)
[Rh(C $\equiv$ CPh){P(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> }]X	2100	(33h)
X = ClO <sub>4</sub> , BF <sub>4</sub> , PF <sub>6</sub>		

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$[\text{Rh}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}(\text{EtOH})]\text{X}_2$ X = $\text{PF}_6$ , $\text{BF}_4$	2115	(33h)
$[\text{Rh}(\text{C}\equiv\text{CPh})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}(\text{OCMe}_2)][\text{PF}_6]_2$	2115	(33h)
$[\text{Rh}(\text{C}\equiv\text{CPh})(\text{H})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$	2115	(88a)
$\text{Rh}(\text{Salen})(\text{C}\equiv\text{CPh})(\text{py})$	2070 <sup>b</sup>	(266)
$\text{RhCp}(\text{C}\equiv\text{CPh})(\text{H})(\text{PPr}^i)_2$	2050 <sup>c</sup>	(270)
$\text{RhCp}(\text{C}\equiv\text{CPh})(\text{HgCl})(\text{PPr}^i)_3$	2097 <sup>c</sup>	(279)
$\text{RhCp}(\text{C}\equiv\text{CPh})(\text{HgI})(\text{PPr}^i)_3$	2096 <sup>c</sup>	(279)
$\text{RhCp}(\text{C}\equiv\text{CPh})(\text{HgMe})(\text{PPr}^i)_3$	2080 <sup>c</sup>	(279)
<i>trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPr}^i)_2$	2090 <sup>q</sup>	(280)
<i>trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2$	2091	(281)
	2118	(272)
	2115	(282a, b)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PCy}_3)_2$	2095 <sup>e</sup>	(271)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$	2127	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{dppe})$	2115 <sup>e</sup>	(271)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\text{CO})(\text{PPh}_3)_2$	2112	(272a)
	2113	(282a)
<i>cis</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{PCy}_3)(\text{cod})$	2090	(93)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{cod})(\text{PPh}_3)_2$	2106	(271)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{cod})(\text{dppe})$	2105	(271)
$\text{Ir}(\text{C}\equiv\text{CPh})_3(\text{PPr}^i)_2$	2080 <sup>c</sup>	(283)
<i>mer,trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})_3(\text{CO})(\text{PPr}^i)_2$	2112, 2157 <sup>c</sup>	(283)
$\text{Ir}(\text{C}\equiv\text{CPh})_2\text{Cl}(\text{PPr}^i)_2$	2105 <sup>c</sup>	(283)
$\text{Ir}(\text{C}\equiv\text{CPh})_2(\text{SnMe}_3)(\text{CO})(\text{PPh}_3)_2$	2122	(272a, b)
$\text{Ir}(\text{C}\equiv\text{CPh})_2(\text{SnMe}_3)(\text{CO})(\text{PMe}_2\text{Ph})_2$	2120	(272a)
<i>cis,trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$	2142	(284)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Br}_2(\text{CO})(\text{PPh}_3)_2$	2137	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{I}_2(\text{CO})(\text{PPh}_3)_2$	2125 <sup>c</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})_2\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}$	2100	(285)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})_2(\text{CO})(\text{dppe})$	2120 <sup>e</sup>	(271)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{SO}_4)(\text{CO})(\text{PPh}_3)_2$	2147 <sup>c</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2$	2133 <sup>c</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{O}_2\text{CMe})_2(\text{CO})(\text{PPh}_3)_2$	2138	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{PPr}^i)_2$	2090 <sup>c</sup>	(286a-c)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{PPr}^i)_2(\text{py})$	2095 <sup>c</sup>	(286c)
<i>mer</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{PPh}_3)_3$	2110	(287)
<i>mer</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{PMePh}_2)_3$	2121	(287)
	2120	(287)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	2128	(272a)
	2119	(287)
	2130 <sup>l</sup>	(282a)
<i>trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{Cl}(\text{CO})(\text{PPr}^i)_2$	2120 <sup>c</sup>	(280)
<i>trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\text{I}(\text{CO})(\text{PPr}^i)_2$	2120 <sup>c</sup>	(280)
<i>trans</i> - $\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})\{\text{OC}(\text{O})\text{CF}_3\}(\text{CO})(\text{PPr}^i)_2$	2120 <sup>c</sup>	(280)
$[\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})_2(\text{PEt}_3)_2][\text{BPh}_4]$	2146 <sup>l</sup>	(282a)
$[\text{Ir}(\text{C}\equiv\text{CPh})(\text{H})(\text{CO})_2(\text{PPh}_3)_2][\text{PF}_6]$	2152	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{ClBr}(\text{CO})(\text{PPh}_3)_2$	2140	(284)



TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	2140	(284)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}(\text{HgCl})(\text{CO})(\text{PPh}_3)_2$	2123 <sup>e</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}(\text{HgCCR})(\text{CO})(\text{PPh}_3)_2$	2120 <sup>c</sup>	(288)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}(\text{OSO}_2\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	2051 <sup>b</sup>	(276)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{Cl}(\text{Me})(\text{CO})(\text{PPh}_3)_2$	2132 <sup>l</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})\text{I}(\text{Me})(\text{CO})(\text{PPh}_3)_2$	2120	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	2125	(282a, b)
	2133	(281)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	2151 <sup>e</sup>	(282a)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\mu\text{-dppm})_2\text{CuCl}$	2100 <sup>c</sup>	(94)
$\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\mu\text{-dppm})_2\text{AgCl}$	2090 <sup>c</sup>	(94)
$[\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\mu\text{-dppm})_2\text{Ag}][\text{BPh}_4]$	2090 <sup>c</sup>	(94)
$\text{K}_2[\text{Ni}(\text{C}\equiv\text{CPh})_4]$	2062	(225)
	2066	(289)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$	2085	(290)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})_2(\text{PBu}^n)_2$	2090	(291)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$	2095	(289)
$\text{Ni}(\text{C}\equiv\text{CPh})_2(\text{PEt}_2\text{Ph})_2$	2088	(292)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PEt}_2\text{Ph})_2$	2098 <sup>a</sup>	(292)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})(\text{C}_6\text{Cl}_5)(\text{PMe}_2\text{Ph})$	2090	(293)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})(\text{C}_6\text{H}_3\text{-2,4,6-Me}_3)(\text{PMe}_2\text{Ph})_2$	2070	(294)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})(\text{C}_6\text{H}_3\text{-2,6-OMe})(\text{PMe}_2\text{Ph})_2$	2078	(294)
<i>trans</i> - $\text{Ni}(\text{C}\equiv\text{CPh})(\text{CCl}=\text{CCl}_2)(\text{PMe}_2\text{Ph})_2$	2083	(294)
$\text{Ni}(\text{C}\equiv\text{CPh})(\text{NO})(\text{PPh}_3)_2$	2090 <sup>b</sup>	(295)
$\text{Ni}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{HgCl}_2$	2080 <sup>e</sup>	(296)
$\text{Ni}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{HgBr}_2$	2080	(296)
$\text{Ni}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{HgI}_2$	2080	(296)
$[\text{Ni}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{Au}]\text{Cl}$	2090	(296)
$\text{NiCp}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$	2160	(222, <sup>b</sup> 297)
	2090 <sup>b</sup>	(298)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2$	2080	(290)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$	2070	(290)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{PMe}_2\text{Ph})_2$	2110 <sup>c</sup>	(299)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$	2110	(290, 299) <sup>c</sup>
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PPh}_3)_2$	2125	(284)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})\text{Br}(\text{PMe}_3)_2$	2118	(300)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})\text{Br}(\text{PPh}_3)_2$	2120	(284)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})(\text{Me})(\text{PMe}_3)_2$	2100 <sup>b</sup>	(301)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$	2113	(302)
<i>trans</i> - $\text{Pd}(\text{C}\equiv\text{CPh})\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PEt}_3)_2$	2100	(303)
<i>cis</i> - $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{dppe})$	2112, 2101	(304)
	2121, 2109 <sup>a</sup>	
<i>cis</i> - $\text{Pd}(\text{C}\equiv\text{CPh})(\text{Me})(\text{dppe})$	2100 <sup>b</sup>	(301)
$\text{Pd}(\text{C}\equiv\text{CPh})_2\{\text{PPh}_2(\text{C}_{10}\text{H}_{14}\text{O})\}_2$	2100	(305)
$\text{Q}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$		
Q = K	2096 <sup>c</sup>	(306)
Q = $\text{NBu}^n_4$	2100	(307)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\text{K}_2[\text{trans-Pt}(\text{C}\equiv\text{CPh})_4(\text{dppe-P})_2]$	2082	(308)
	2092, 2109 <sup>b,o</sup>	
$[\text{PMePh}_3]_2[\text{cis-Pt}(\text{C}\equiv\text{CPh})_2(\text{C}_6\text{F}_5)_2]$	2083, 2096	(302)
$[\text{PMePh}_3]_2[\text{Pt}(\text{C}\equiv\text{CPh})_3(\text{C}_6\text{F}_5)]$	2076, 2100	(309)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2$	2090	(290)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$	2107	(290,310)
	2100	(311)
	2105 <sup>c</sup>	(312)
	2103 <sup>b</sup>	(21)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PBu}^n)_2$	2100	(310)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMe}_2\text{Ph})_2$	2106	(313)
	2116	(314)
	2110	(315)
	2100	(316)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMePh}_2)_2$	2105	(307)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$	2090	(290)
	2110	(317a,b)
	2120	(318)
	2100 <sup>b</sup>	(218)
	2130	(319)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-P})_2$	2105	(307)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)$	2100	(307)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{SbEt}_3)_2$	2080	(290)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PEt}_3)_2$	2120	(106)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PEt}_2\text{Ph})_2$	2120	(320)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PMePh}_2)_2$	2130	(320,321) <sup>r</sup>
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\text{Cl}(\text{PPh}_3)_2$	2125	(317b)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\text{I}(\text{PPh}_3)_2$	2125	(284)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{Me})(\text{PMe}_3)_2$	2100 <sup>b</sup>	(301)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{C}_6\text{H}_4\text{-3-F})(\text{PEt}_3)_2$	2105 <sup>p</sup>	(30)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{C}_6\text{H}_4\text{-4-F})(\text{PEt}_3)_2$	2110 <sup>p</sup>	(30)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{CPh}=\text{CH}_2)(\text{PPh}_3)_2$	2110	(119)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PEt}_3)_2$	2100	(303)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{CMe}=\text{CH}_2)(\text{PPh}_3)_2$	2102 <sup>c</sup>	(118,128)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{SnMe}_3)(\text{PMePh}_2)_2$	2110	(272a,b)
<i>trans</i> - $\text{Pt}(\text{C}\equiv\text{CPh})(\text{SnMe}_3)(\text{PPh}_3)_2$	2100	(272a,b)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$	2106, 2113	(310)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PBu}^n)_2$	2098, 2110	(310)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PMePh}_2)_2$	2120, 2130 <sup>c</sup>	(321)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$	2125	(113,317b)
	2110 <sup>c</sup>	(321)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm})$	2108 <sup>c</sup>	(322)
<i>cis</i> - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppe})$	2112 <sup>c</sup>	(322)
	2110	(316)
	2116	(314)
	2095, 2110	(308)
	2098, 2116 <sup>c</sup>	(308)
	2098, 2112 <sup>b,o</sup>	(308)

(continued)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ (cm <sup>-1</sup> )	Ref.
<i>cis</i> -Pt(C≡CPh) <sub>2</sub> (cod)	2130, 2135 <sup>c</sup>	(321)
<i>cis</i> -Pt(C≡CPh)Cl(PPh <sub>3</sub> ) <sub>2</sub>	2125	(284)
<i>cis</i> -Pt(C≡CPh)Br(PPh <sub>3</sub> ) <sub>2</sub>	2125	(284,323)
<i>cis</i> -Pt(C≡CPh)I(PPh <sub>3</sub> ) <sub>2</sub>	2125	(284)
<i>cis</i> -Pt(C≡CPh)Me(dppe)	2110	(186a)
<i>cis</i> -Pt(C≡CPh)(C <sub>6</sub> F <sub>5</sub> )(dppe)	2116	(302)
<i>cis</i> -Pt(C≡CPh)(SnPh <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2100 <sup>b</sup>	(324)
Pt(C≡CPh) <sub>2</sub> {PPh <sub>2</sub> (C <sub>10</sub> H <sub>14</sub> O)} <sub>2</sub>	2105 <sup>c</sup>	(305)
Pt(C≡CPh)Cl(PEt <sub>3</sub> ) <sub>2</sub>	2120 <sup>c</sup>	(312)
Pt(C≡CPh)(SnEt <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2108	(272a,b)
Pt(C≡CPh)(C <sub>6</sub> F <sub>5</sub> )(py)(PPh <sub>3</sub> )	2118	(325)
[Pt(C≡CPh)(AsMe <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	2100 <sup>b</sup>	(326)
[Pt(C≡CPh)(CN-C <sub>6</sub> H <sub>4</sub> -4-OMe)(PMePh <sub>2</sub> )] [PF <sub>6</sub> ]	2145	(320)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz-3,5-Me <sub>2</sub> )Rh(CO)] [PF <sub>6</sub> ]	2129	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz-4-Me <sub>2</sub> )Rh(CO)] [PF <sub>6</sub> ]	2126	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz)Rh(CO)] [PF <sub>6</sub> ]	2122	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz-4-Br-3,5-Me <sub>2</sub> )Rh(CO)] [PF <sub>6</sub> ]	2122	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz-3,4,5-Br <sub>3</sub> )Rh(CO)] [PF <sub>6</sub> ]	2133	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-pz-3-Me-5-CF <sub>3</sub> )Rh(CO)] [PF <sub>6</sub> ]	2129	(137)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)Ir(SO <sub>2</sub> )	2104	(327)
Pt(C≡CPh) <sub>2</sub> (μ-dppm) <sub>2</sub> (μ-SO <sub>2</sub> )[IrCl]	2103	(327)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-SO <sub>2</sub> )(μ-C≡CPh)RhCl	2105	(327)
Pt <sub>2</sub> (C≡CPh)(PPr <sup>i</sup> <sub>2</sub> Ph) <sub>2</sub> (μ-C≡CPh)(μ-SiMe <sub>2</sub> )	2108	(145)
Pt <sub>2</sub> (C≡CPh)(PCy <sub>3</sub> ) <sub>2</sub> (μ-C≡CPh)(μ-SiMe <sub>2</sub> )	2100	(145)
Pt <sub>2</sub> (C≡CPh)(PMeBu <sup>i</sup> ) <sub>2</sub> (μ-C≡CPh)(μ-SiMe <sub>2</sub> )	2104	(145)
[Pt(C≡CPh){C(NHBu <sup>n</sup> )NH(C <sub>6</sub> H <sub>4</sub> -4-OMe)}(PMePh <sub>2</sub> )] [PF <sub>6</sub> ]	2130	(320)
[PMePh <sub>3</sub> ] <sub>2</sub> [Pt(C≡CPh)(C <sub>6</sub> F <sub>5</sub> )(μ-C≡CPh) <sub>2</sub> Pt(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ]	2109	(309)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)W(CO) <sub>3</sub>	2110 <sup>c</sup>	(132a)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)Mo(CO) <sub>3</sub>	2120	(132a)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CHPh)W(CO) <sub>3</sub>	2120	(132a)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)IrCl	2112	(328)
Pt(C≡CPh) <sub>2</sub> (μ-dppm) <sub>2</sub> (μ-H)Ir(H)Cl	2118	(328)
Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)Ir(CO)Cl	2102	(328)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)Ir(CO)] [BPh <sub>4</sub> ]	2125	(328)
[Pt(C≡CPh)(μ-dppm) <sub>2</sub> (μ-C≡CPh)Pt(C≡CPh)] [ClO <sub>4</sub> ]	2120	(20a)
[ <i>trans</i> -Pt(C≡CPh)(NH=NC <sub>6</sub> H <sub>4</sub> -4-F)(PPh <sub>3</sub> ) <sub>2</sub> ] [BF <sub>4</sub> ]	2124 <sup>b</sup>	(123)
[Pt <sub>2</sub> (C≡CPh)(PEt <sub>3</sub> ) <sub>4</sub> (μ-C≡CHPh)] [BF <sub>4</sub> ]	2100 <sup>c</sup>	(144)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )Cl}	2115 <sup>g</sup>	(20c)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )Br}	2115 <sup>g</sup>	(20c)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )I}	2115 <sup>g</sup>	(20c)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )(SPh)}	2110 <sup>g</sup>	(20c)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )(SCHMe <sub>2</sub> )}	2115 <sup>g</sup>	(20c)
Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> (μ-C≡CHPh){Pt(PEt <sub>3</sub> )(SCl <sub>3</sub> )}	2110 <sup>g</sup>	(20c)
[Pt(C≡CPh)(PEt <sub>3</sub> ) <sub>2</sub> {μ-η <sup>2</sup> ,η <sup>4</sup> -C(Ph)=CC(Ph)CH(Ph)}Pt(PEt <sub>3</sub> ) <sub>2</sub> ] [BF <sub>4</sub> ]	2108 <sup>c</sup>	(139)
Pt(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> {N(C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub> )NNN(C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub> )}	2154 <sup>c</sup>	(131)
{Pt(C≡CPh)} <sub>2</sub> (μ-H)(μ-dppm) <sub>2</sub>	2110 <sup>c</sup>	(329)
Pt <sub>2</sub> (C≡CPh) <sub>2</sub> (μ-dppm) <sub>2</sub>	2090 <sup>c</sup>	(329)
{Pt(C≡CPh)} <sub>2</sub> (μ-CS <sub>2</sub> )(μ-dppm) <sub>2</sub>	2110 <sup>c</sup>	(329)

TABLE VI (continued)

Compound	$\nu(\text{C}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	Ref.
$\{\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\mu\text{-dppm})_2$	2110 <sup>c</sup>	(329)
<i>trans</i> - $\{\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2$	2105	(307)
$[\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{Ag}][\text{PF}_6]$	2105 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{AgI}$	2105 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{AgCl}$	2105 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})\text{Cl}(\mu\text{-dppm})_2\text{AgCl}$	2120 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})\text{Br}(\mu\text{-dppm})_2\text{AgBr}$	2120 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})\text{I}(\mu\text{-dppm})_2\text{AgI}$	2109 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{CuCl}$	2110 <sup>c</sup>	(330)
$[\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{Cu}][\text{BPh}_4]$	2130 <sup>c</sup>	(330)
$\text{Pt}(\text{C}\equiv\text{CPh})_2(\mu\text{-dppm})_2\text{HgCl}_2$	2102, 2114	(307)
$\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2(\mu\text{-C}\equiv\text{CPh})\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})$	2127 <sup>b</sup>	(143)
$\text{Pt}(\text{C}\equiv\text{CPh})(\text{PEt}_3)_2(\mu\text{-C}\equiv\text{CPh})\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})$	2128 <sup>b</sup>	(143)
$[\text{Q}][\text{Au}(\text{C}\equiv\text{CPh})_2]$		
Q = $\text{NBu}^n_4$	2105	(32)
Q = $\text{N}(\text{PPh}_3)_2$	2105 <sup>b</sup>	(331)
Q = $\text{PPh}_4$	2102	(32)
Q = K	2102 <sup>c</sup>	(332)
	2112 <sup>c,o</sup>	(332)
	2110 <sup>c</sup>	(333)
$\text{Au}(\text{C}\equiv\text{CPh})(\text{PMe}_3)$	2097 <sup>b</sup>	(148)
	2102 <sup>c</sup>	(334)
$\text{Au}(\text{C}\equiv\text{CPh})(\text{PPr}^i_3)$	2102 <sup>c</sup>	(334)
$\text{Au}(\text{C}\equiv\text{CPh})(\text{PCy}_3)$	2113 <sup>b</sup>	(335)
$\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$	2118 <sup>c</sup>	(336)
	2120 <sup>b</sup>	(148)
	2125	(32)
$\text{Au}(\text{C}\equiv\text{CPh})\{\text{P}(p\text{-Tol})_3\}$	2120 <sup>c</sup>	(336)
$\text{Au}(\text{C}\equiv\text{CPh})\{\text{PPh}(\text{OMe})_2\}$	2110 <sup>b</sup>	(148)

<sup>a</sup> Frequencies are given in  $\text{cm}^{-1}$ . Unless noted otherwise, frequencies were determined by infrared spectroscopy for nujol mull samples.

<sup>b</sup> Sample type not reported.

<sup>c</sup> KBr pellet.

<sup>d</sup> Halocarbon mull.

<sup>e</sup>  $\text{CH}_2\text{Cl}_2$  solution.

<sup>f</sup> Cyclohexane solution.

<sup>g</sup> Hexane solution.

<sup>h</sup> Neat.

<sup>i</sup> Toluene solution.

<sup>j</sup>  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{D}_6$  solution.

<sup>k</sup> Tetrahydrofuran solution.

<sup>l</sup>  $\text{CHCl}_3$  solution.

<sup>m</sup> *N*-Methylpyrrolidone solution.

<sup>n</sup> Pyridine solution.

<sup>o</sup> From Raman spectroscopy.

<sup>p</sup>  $\text{CCl}_4$  solution.

<sup>q</sup> Pentane solution.

cases where they have been studied. Nearly all  $\nu(\text{C}\equiv\text{C})$  frequencies have been measured by infrared spectroscopy.

Before discussing the distribution of  $\nu(\text{C}\equiv\text{C})$  frequencies for metal-alkynyl compounds, we make note of two caveats. First, it is clear that there are complexes in Table VI for which incorrect frequencies have been reported. A particularly egregious example is the simple compound *trans*-Pt(C $\equiv$ CPh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, for which  $\nu(\text{C}\equiv\text{C})$  frequencies of 2090 (290), 2100 (218), 2110 (317*a,b*), 2120 (318), and 2130 (319) cm<sup>-1</sup> are claimed. This particular problem is easy to spot. But because for most metal-alkynyl complexes there has only been a single frequency measurement, incorrect data for them may not stand out, and the  $\nu(\text{C}\equiv\text{C})$  frequency distribution may be skewed accordingly by their inclusion in it. We have not corrected frequencies that we suspect have been misassigned, because this could only legitimately be done by inspecting the vibrational spectra, which are very rarely presented. We believe errors should be apparent by being grossly outlying points in the distribution and by comparison to frequencies of related complexes.

A second cautionary note regards the  $\nu(\text{C}\equiv\text{C})$  frequencies of complexes with two or more chemically equivalent alkynyl ligands. Depending on the symmetry of the compound, the spectra of these species may exhibit more than one  $\nu(\text{C}\equiv\text{C})$  band, because the  $\nu(\text{C}\equiv\text{C})$  modes consist of different symmetry-adapted combinations of the various C $\equiv$ C stretching coordinates. An example is the compound *cis*-Pt(C $\equiv$ CPh)<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub> (310), for which  $\nu(\text{C}\equiv\text{C})$  infrared bands at 2098 and 2110 cm<sup>-1</sup> are observed. However, many such compounds are reported to exhibit only a single  $\nu(\text{C}\equiv\text{C})$  band (e.g., *cis*-Pt(C $\equiv$ CPh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) (113, 317*b*, 321), even when other  $\nu(\text{C}\equiv\text{C})$  modes are dipole allowed. In drawing comparisons among the frequencies of bis-alkynyl (and more highly substituted alkynyl) complexes, it is important to compare frequencies for modes of identical symmetry only; reference to Table VI reveals that  $\nu(\text{C}\equiv\text{C})$  modes of different symmetry can vary by 5–45 cm<sup>-1</sup> within a single compound, and “shifts” of this magnitude could easily be misinterpreted as being the result of differences in M–CCR  $\pi$ -bonding. This complication would seem to be particularly acute for metal-alkynyl polymers (4*a–e*).

The distribution of C $\equiv$ C stretching frequencies for the L<sub>*n*</sub>M–C $\equiv$ CPh complexes set out in Table VI is displayed in Fig. 5. In those cases where several different frequencies are reported for the same compound, we chose the one that was most often reported [e.g., 2120 cm<sup>-1</sup> for *trans*-Ir(C $\equiv$ CPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>]; if a “consensus frequency” was unavailable [e.g., *trans*-Pt(C $\equiv$ CPh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], the compound was excluded. The C $\equiv$ C frequencies of metal-phenylethynyl complexes span a roughly 180 cm<sup>-1</sup> range, although 98% of them lie in the range 2030–2160 cm<sup>-1</sup>.

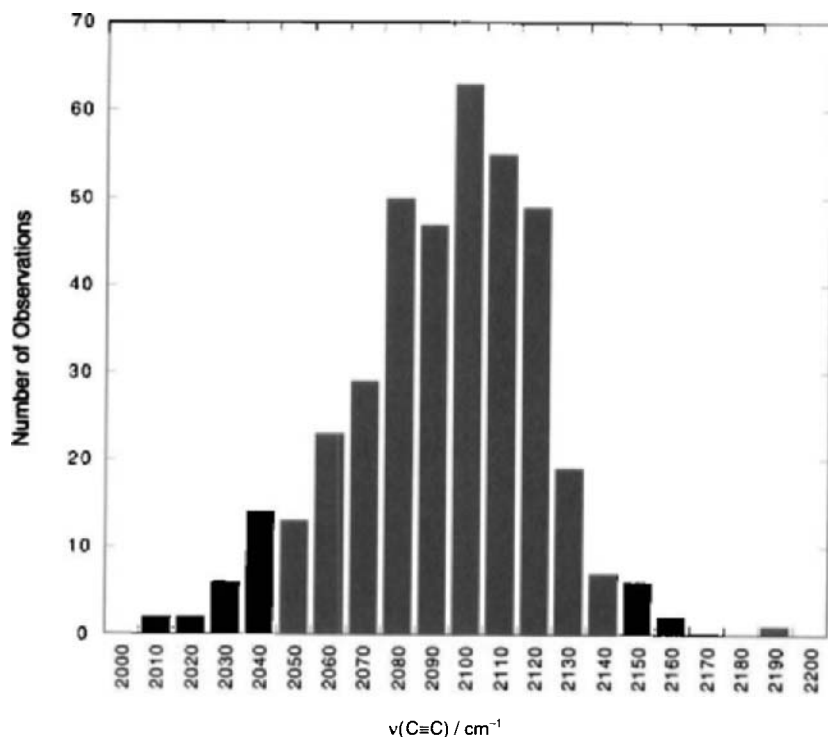


FIG. 5. Distribution of  $\text{C}\equiv\text{C}$  stretching frequencies for  $\text{L}_n\text{M}-\text{C}\equiv\text{CPh}$  complexes. Data are taken from Table VI. The frequency labels correspond to the centers of the bins.

As for the  $\text{C}\equiv\text{C}$  bond distances of metal-alkynyl complexes (Section III-B), the interpretation of  $\nu(\text{C}\equiv\text{C})$  frequencies requires a reference point; and while terminal alkynes are commonly used in this regard, they are flawed because the  $\nu(\text{C}\equiv\text{C})$  mode contains contributions from the terminal  $\text{C}-\text{H}$  coordinate (207). Better reference compounds are organic and main-group phenylethyne derivatives of type  $\text{RC}\equiv\text{CPh}$  ( $\text{R} \neq \text{H}$ ), for which  $\nu(\text{C}\equiv\text{C})$  frequencies range from  $2150\text{--}2280\text{ cm}^{-1}$  ( $\text{R} = \text{Me}, t\text{-Bu}, \text{CH}_2\text{OH}, \text{CHO}, \text{CO}_2\text{H}, \text{NMe}_2, \text{SiMe}_3, \text{SMe}, \text{Cl}, \text{Br}, \text{I}$ ); by comparison,  $\nu(\text{C}\equiv\text{C}) = 2111\text{ cm}^{-1}$  for phenylacetylene (207). The fact that the  $\nu(\text{C}\equiv\text{C})$  frequencies for  $\text{L}_n\text{M}-\text{C}\equiv\text{CPh}$  complexes are lower than those of  $\text{RC}\equiv\text{CPh}$  compounds is consistent with the observation that the  $\text{C}\equiv\text{C}$  bond distances of metal-alkynyl complexes are longer than those of disubstituted organic alkynes. The two possible explanations put forth previously for the  $\text{C}\equiv\text{C}$  bond distances (Section III-B) apply here as well, that is, that the difference between the  $\text{C}\equiv\text{C}$  bonds of organic alkynes

and metal-alkynyl compounds reflects the effects of  $M \rightarrow CCR$   $\pi$ -backbonding (or  $RCC \rightarrow M$   $\pi$ -bonding) and/or that the  $M-CCR$  bond is polarized in a  $M^{\delta+}-C^{\delta-}$  fashion—although the greater precision of the  $\nu(C\equiv C)$  frequencies allows these possibilities to be addressed in more detail than was possible for the  $C\equiv C$  bond distances.

Some of the trends in  $\nu(C\equiv C)$  frequencies among the compounds in Table VI would appear to be consistent with  $M \rightarrow CCR$   $\pi$ -backbonding. Within a set of  $L_n M-C\equiv CPh$  complexes of a given metal, shifts in the frequency of  $\nu(C\equiv C)$  upon changing the electron donating or accepting characteristics of the ancillary ligands are typically observed to be in the expected direction, with lower frequencies being found for electron-rich metal centers; the magnitudes of these shifts are modest ( $<50\text{ cm}^{-1}$ ). Some selected, relatively simple examples of this effect include the pairs of compounds and ions  $[W(C\equiv CPh)(CO)_4L]^-$  ( $L = CO$ ,  $\nu(C\equiv C) = 2080\text{ cm}^{-1}$ ;  $L = PPh_3$ ,  $\nu(C\equiv C) = 2065\text{ cm}^{-1}$ ) (213),  $FeCp^*(C\equiv CPh)L_2$  ( $L = CO$ ,  $\nu(C\equiv C) = 2095\text{ cm}^{-1}$  (59);  $L = \frac{1}{2}\text{ dppe}$ ,  $\nu(C\equiv C) = 2054\text{ cm}^{-1}$  (33*o*), and *trans*- $Pd(C\equiv CPh)X(PMe_3)_2$  ( $X = Me$ ,  $\nu(C\equiv C) = 2100\text{ cm}^{-1}$  (301);  $X = Br$ ,  $\nu(C\equiv C) = 2118\text{ cm}^{-1}$  (300). Ancillary ligands with less dramatic electronic differences than these yield smaller frequency shifts; for example, phenylethynyl complexes with ancillary phosphine ligands that differ in their R-groups commonly exhibit identical  $\nu(C\equiv C)$  frequencies. To the extent that the electronic characteristics of the metal center that favor  $M \rightarrow CCR$   $\pi$ -backbonding tend to disfavor  $RCC \rightarrow M$   $\pi$ -bonding, it is less clear how to reconcile these trends in frequencies within the framework of the latter model of metal-alkynyl bonding, with the data for  $FeCp^*(C\equiv CPh)L_2$  ( $L = CO$ ,  $\frac{1}{2}\text{ dppe}$ )—the class of compounds from which theoretical (11) and photoelectron-spectroscopic (12*a,b*) studies yielded the  $RCC \rightarrow M$   $\pi$ -bonding model—standing out in this regard.

Another probe of the extent of  $M \rightarrow CCR$   $\pi$ -backbonding is the sensitivity of the  $\nu(C\equiv C)$  frequency to the oxidation state of the metal. But because the  $M-CCR$  bond polarity should also be quite sensitive to the metal oxidation state, an unambiguous interpretation of these data cannot be devised straightforwardly. From the standpoint of  $M \rightarrow CCR$   $\pi$ -backbonding, the simple expectation is that the  $\nu(C\equiv C)$  frequency should decrease according to  $M^{(n+1)+} \geq M^{n+}$ . This expectation is not always fulfilled. Consistent with this ordering, Bianchini, Zanello, and co-workers have reported tandem electrochemical and vibrational-spectroscopic studies on compounds of the general form  $[M(C\equiv CR)\{E(CH_2CH_2PPh_2)_3\}]^{n+}$  ( $M = Fe, Co, Rh$ ;  $E = N, P$ ), for which they found the  $\nu(C\equiv C)$  frequencies to be ordered  $Co^{II} > Co^I$  (33*j*,82),  $Rh^{III} > Rh^{II} > Rh^I$  (33*h,m,88a,b,277,278*), and  $Fe^{III} \cong Fe^{II}$  (33*a,235*). This was interpreted as suggesting that  $M \rightarrow CCR$   $\pi$ -backbonding is present in the  $Co^I$ ,  $Rh^I$ ,

and  $\text{Rh}^{\text{II}}$  compounds but is unimportant for the iron compounds. Similarly, Bear *et al.* concluded that  $\text{M} \rightarrow \text{CCH} \pi$ -backbonding is present in the series of complexes  $[\text{Rh}_2(\text{C}\equiv\text{CH})(\mu\text{-NC}_5\text{H}_4\text{-2-NPh})_4]^{-/0/+}$  based on the observation that the  $\nu(\text{C}\equiv\text{C})$  frequencies decrease by 18 and  $32 \text{ cm}^{-1}$  on one- and two-electron reduction, respectively, relative to that of the cation (33i). In sharp contrast to these studies are reports of two compounds for which  $\nu(\text{C}\equiv\text{C})$  decreases upon an increase in metal oxidation state. Whiteley and co-workers discovered that the  $\nu(\text{C}\equiv\text{C})$  frequencies of the  $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}\equiv\text{CR})(\text{dppe})]^+$  ( $\text{R} = \text{Ph}, t\text{-Bu}$ ) ions are  $13 \text{ cm}^{-1}$  lower than those of the neutral compounds (33g,n), and independent data from Connelly *et al.* and Whiteley *et al.* reveal that for the pair of compounds  $[\text{FeCp}^*(\text{C}\equiv\text{CPh})(\text{dppe})]^{0/+}$ , the  $\nu(\text{C}\equiv\text{C})$  frequencies lie in the order  $\text{Fe}^{\text{III}}$  ( $2022 \text{ cm}^{-1}$ ) (33d) <  $\text{Fe}^{\text{II}}$  ( $2054 \text{ cm}^{-1}$ ) (33o). These latter results are clearly inconsistent with the HOMO's of these compounds participating in  $\text{Fe} \rightarrow \text{CCR} \pi$ -backbonding. The frequency shifts of  $[\text{FeCp}^*(\text{C}\equiv\text{CPh})(\text{dppe})]^{0/+}$  could be viewed as supporting the presence of  $\text{RCC} \rightarrow \text{Fe} \pi$ -bonding, as proposed in theoretical and photoelectron-spectroscopic studies of related compounds (11, 12a,b).

In none of the cases just described do the differences in  $\nu(\text{C}\equiv\text{C})$  frequencies among a series of redox congeners or analogous  $\text{L}_n\text{M}-\text{C}\equiv\text{CPh}$  complexes of a given metal exceed more than one-third of the  $150\text{-cm}^{-1}$  or so range of frequencies exhibited in Fig. 5. This raises the additional question of the role of the nature of the metal in determining this frequency, through its potential influences on both  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding and on  $\text{M}-\text{CCR}$  bond polarity. Both of these interpretations have been invoked previously to explain trends in  $\nu(\text{C}\equiv\text{C})$  frequencies as a function of metal. In papers in which it is presumed that  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding is a general feature of metal-alkynyl compounds, differences in  $\nu(\text{C}\equiv\text{C})$  frequencies among analogous  $\text{L}_n\text{M}-\text{C}\equiv\text{CPh}$  complexes of different metals have been used to order the metals according to their  $\pi$ -basicity. Systematic differences in the frequency of  $\nu(\text{C}\equiv\text{C})$  as a function of metal are not always observed, however: the frequencies of the complexes *trans*- $\text{M}(\text{C}\equiv\text{CPh})_2(\text{PET}_3)_2$  stand in the order  $\text{Pt}$  ( $2107 \text{ cm}^{-1}$ ) >  $\text{Ni}$  ( $2085 \text{ cm}^{-1}$ ) >  $\text{Pd}$  ( $2070 \text{ cm}^{-1}$ ) (290), while those of  $[\text{M}(\text{C}\equiv\text{CPh})(\text{CO})_5]^-$  are independent of metal ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\nu(\text{C}\equiv\text{C}) = 2080 \text{ cm}^{-1}$ ) (213). Moreover, the  $\nu(\text{C}\equiv\text{C})$  frequencies of the  $d^0$  complexes  $\text{MCp}_2(\text{C}\equiv\text{CPh})_2$  are also metal-sensitive, varying according to  $\text{Hf}$  ( $2080 \text{ cm}^{-1}$ ) (35) >  $\text{Zr}$  ( $2075 \text{ cm}^{-1}$ ) (35) >  $\text{Ti}$  ( $2070 \text{ cm}^{-1}$ ) (208a,b), even though  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding must be absent. That  $\nu(\text{C}\equiv\text{C})$  frequencies cannot, in general, be interpreted exclusively within a  $\text{L}_n\text{M} \rightarrow \text{CCR} \pi$ -backbonding framework suggests that they are also governed by bond-polarity considerations, as we noted earlier for the interpretation of  $\text{C}\equiv\text{C}$  bond lengths (Section III-B). Nast



has noted that the bond-polarity explanation finds support among alkali-metal  $M-C\equiv CPh$  complexes (*I*), the  $\nu(C\equiv C)$  frequencies of which range from  $1990\text{ cm}^{-1}$  ( $M = Rb, Cs$ ) to  $2036\text{ cm}^{-1}$  ( $M = Li$ ) (337). In interpreting these latter frequencies, however, allowance must be made for the fact

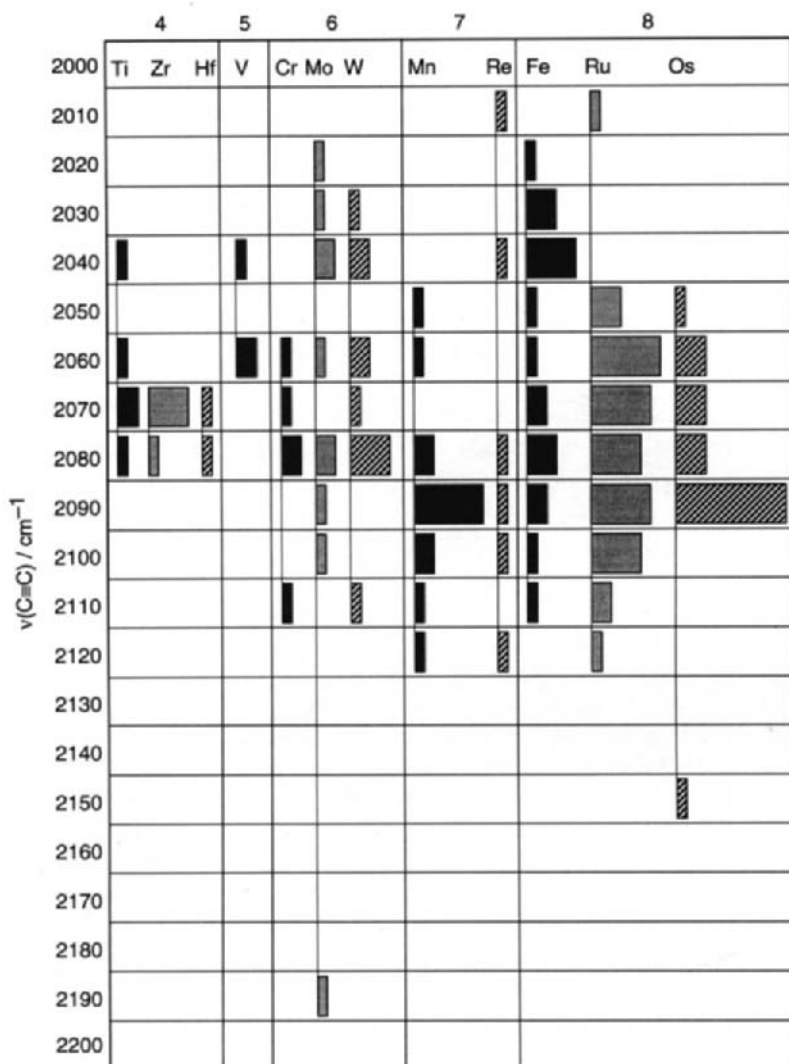


FIG. 6. Distribution of  $C\equiv C$  stretching frequencies for  $L_nM-C\equiv CPh$  complexes broken down according to metal. Data are taken from Table VI. The frequency labels correspond to the centers of the bins.



tions, arranged by group. There are too few data for the complexes of groups 4–7 to draw any definitive conclusions regarding global trends in the frequencies, but several tentative observations can be advanced. First, there appears to be a gradual increase in the frequency of  $\nu(\text{C}\equiv\text{C})$  from left to right across the transition series. Choosing  $2100\text{ cm}^{-1}$  as a reference frequency, one notes that the majority of  $\nu(\text{C}\equiv\text{C})$  frequencies for compounds in groups 4–8 are  $<2100\text{ cm}^{-1}$ , while those for iridium, palladium, platinum, and gold are  $>2100\text{ cm}^{-1}$ . Second, the data for compounds of the groups 9 and 10 metals suggest that  $\nu(\text{C}\equiv\text{C})$  frequencies increase down a group. There are obviously insufficient data for the early metals to comment on the generality of this trend, nor is it clear that the data for osmium are consistent with it. On the whole, though, these trends appear to be more consistent with M–CCR bond polarity being the stronger influence on the frequency of  $\nu(\text{C}\equiv\text{C})$  than is  $\text{M} \rightarrow \text{CCR} \pi$ -backbonding, because  $\nu(\text{C}\equiv\text{C})$  shifts to lower frequency for the more electropositive metals, with their typically lower *d*-electron counts. Much additional data for the early metals will be required before it is apparent whether these observations find support or whether they are merely a result of the small sample size. Nonetheless, it is clear that differences between the  $\nu(\text{C}\equiv\text{C})$  frequencies of compounds from different groups of the transition series should be interpreted with caution.

In closing, we emphasize that, because this discussion has been limited to complexes of the phenylethynyl ligand, it would not be appropriate to treat these observations as general for complexes of other alkynyl ligands, particularly those with R-groups whose electron donor or acceptor characteristics are significantly different from those of phenyl. Moreover, the phenyl group has a considerable electronic  $\pi$ -buffering capability, which may partially mask the intrinsic behavior of the  $\text{C}\equiv\text{C}$  bond in these data.

### C. M–C and C–R Stretching Frequencies

Few M–C stretching frequencies have been reported for metal–alkynyl complexes (15*d*, 289, 290, 310, 339). The only detailed investigation has been that of Masai *et al.* on *trans*- $\text{M}(\text{C}\equiv\text{CR})_2\text{L}_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{R} = \text{Me}, \text{CH}_2\text{F}, \text{Ph}, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CH}, \text{C}\equiv\text{CPh}$ ;  $\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PPh}_3, \text{SbEt}_3$ ) complexes (290). Comparisons among the infrared spectra of these compounds suggested assignment of a band in the  $535\text{--}600\text{ cm}^{-1}$  region as the  $b_{2u}$ -symmetry  $\nu(\text{M}–\text{C})$  mode. The frequency of this mode depends strongly on the nature of the alkynyl R-group and weakly on the nature of M and L. Interestingly, the squares of the M–C frequencies ( $\nu^2$ ) of these compounds are a linear function of the Taft  $\sigma^*$  constant of the R-group.

By assuming that  $\nu(\text{M}-\text{C})$  contains negligible contributions from other symmetry coordinates and that  $\nu^2$  reflects the  $\text{M}-\text{C}$  bond strength (via their relationship to the force constant), these workers concluded that the  $\text{M}-\text{C}$  bond is strengthened with the increasing electronegativity of the  $\text{R}$ -group. This was interpreted as resulting from enhanced  $\text{M} \rightarrow \text{CCR}$   $\pi$ -backbonding in compounds with  $\text{R}$ -groups of greatest electronegativity.

The only alkynyl complexes for which  $\nu(\text{C}-\text{R})$  frequencies are routinely reported are those of the parent ethynyl ligand,  $\text{C}\equiv\text{CH}$  [ $\nu(\text{C}-\text{H}) = 3250\text{--}3300\text{ cm}^{-1}$ ]. Bell and Chisholm reported infrared-spectroscopic frequencies for the natural-abundance and deuterium-labeled pairs of complexes *trans*- $\text{Pt}(\text{C}\equiv\text{CH}/\text{D})_2(\text{PMe}_2\text{Ph})_2$  and *trans*- $\text{Pt}(\text{C}\equiv\text{CH}/\text{D})\text{X}(\text{PMe}_2\text{Ph})_2$  ( $\text{X} = \text{Cl}, \text{CCl}=\text{CH}_2/\text{D}_2$ ); the alkynyl  $\nu(\text{C}-\text{H})$  and  $\nu(\text{C}-\text{D})$  infrared bands appear at ca.  $3280\text{ cm}^{-1}$  and  $2550\text{ cm}^{-1}$ , respectively, with the  $\nu(\text{C}\equiv\text{C})$  frequencies of these isotopomers being approximately  $1970\text{ cm}^{-1}$  for  $\text{C}\equiv\text{CH}$  and  $1850\text{ cm}^{-1}$  for  $\text{C}\equiv\text{CD}$  (340).

## V

### CONCLUDING REMARKS

Viewed as a whole, it appears that the results of the structural, spectroscopic, theoretical, and other physical studies on metal-alkynyl complexes cannot be interpreted within a single, simple picture of the nature of metal-alkynyl bonding. In view of the fact that understanding the electronic-structural basis of the reactions of metal-alkynyl complexes and the physical properties of the advanced materials developed from them requires a clear picture of this bond, further work in this area would be highly desirable. Of particular value would be studies that applied a combination of the experimental techniques described above and theoretical calculations to a series of archetypal metal-alkynyl complexes from across the transition series, so as both to gauge the effect of the metal on the nature of the  $\text{M}-\text{CCR}$  bond and to clarify the benchmark parameters for each technique within different metal-alkynyl bonding regimes.

The history of routinely interpreting the structures and spectra of metal-carbonyl and -cyano complexes from a  $\pi$ -backbonding perspective tempts one to carry this approach over to metal-alkynyl complexes as well. But however successful this may appear to be for individual or limited series of metal-alkynyl compounds, consideration of the whole body of metrical and vibrational-frequency data associated with the  $\text{M}-\text{C}\equiv\text{C}-\text{R}$  linkage makes it clear that, rather than a particular datum or series of data demonstrating the presence of  $\pi$ -backbonding, they are

probably no more than just consistent with it, the frequent, less equivocal claims in the literature notwithstanding. Different experimental techniques sometime lead to different conclusions about the nature of this bond for a single compound. The bond distances and vibrational frequencies of metal–alkynyl compounds should be interpreted with this point in mind.

## VI

### APPENDIX: ABBREVIATIONS USED IN THIS REVIEW

bpy	2,2'-bipyridine
cod	cycloocta-1,5-diene
Cp	$\eta^5\text{-C}_5\text{H}_5$
Cp*	$\eta^5\text{-C}_5\text{Me}_5$
Cy	cyclohexyl
dbpe	1,2-bis(di- <i>n</i> -butylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	1,2-bis(diphenylphosphino)methane
dppp	1,2-bis(diphenylphosphino)propane
HOMO	highest-occupied molecular orbital
LUMO	lowest-unoccupied molecular orbital
MLCT	metal-to-ligand charge transfer
N <sub>4</sub>	3,9-dimethyl-4,8-diazaundecane-2,10-dione dioxime
Pc	phthalocyaninato
phen	1,10-phenanthroline
PPN	N(PPh <sub>3</sub> ) <sub>2</sub>
py	pyridine
pzH	pyrazole
Salen	<i>N,N'</i> -bis(salicylaldehydo)ethylenediamine
Tol	tolyl
Tp'	hydrotris(3,5-dimethylpyrazolyl)borato
TPP	tetraphenylporphyrin dianion

### ACKNOWLEDGMENT

We are indebted to the National Science Foundation for their support of our research through Grant CHE 93-07013. M.D.H. gratefully acknowledges support through fellowships from the David and Lucile Packard Foundation and the Alfred P. Sloan Foundation. We thank John Cooper, Tara Meyer, Joe Grabowski, and colleagues at other institutions for

bringing various papers to our attention. We are especially grateful to Todd Marder for providing us with preprints and unpublished crystallographic data.

## REFERENCES

- (1) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.
- (2) Recent leading references to this work from various research groups include
- (2a) Chiang, S.-J.; Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1994**, *116*, 11181.
- (2b) Akita, M.; Sugimoto, S.; Takabuchi, A.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1993**, *12*, 2925.
- (2c) Lang, H.; Herres, M.; Zsolnai, L. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 429.
- (2d) Berenguer, J. R.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1993**, *12*, 6.
- (2e) Weidmann, T.; Weinrich, V.; Wagner, B.; Robl, C.; Beck, W. *Chem. Ber.* **1991**, *124*, 1363.
- (2f) Bruce, M. I.; Koutsantonis, G. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *407*, 391.
- (2g) Lotz, S.; van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219.
- (3) Werner, H. *Nachr. Chem., Tech. Lab.* **1992**, *40*, 435; Bruce M. I. *Chem. Rev.* **1991**, *91*, 197; *Pure Appl. Chem.* **1990**, *62*, 1021; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077; Bruce, M. I. *J. Organomet. Chem.* **1990**, *400*, 321; Pombeiro, A. J. L.; Richards, R. L. *Coord. Chem. Rev.* **1990**, *104*, 13; Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1; Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1989**, *58*, 693; Pombeiro, A. J. L. *Polyhedron* **1989**, *8*, 1595; Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761; Bruce, M. I. *Pure Appl. Chem.* **1986**, *58*, 553; Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
- (4a) Dick, G. S. S.; Marder, T. B.; Khan, M. S.; Kakkar, A. K.; Lewis, J. Review article in preparation.
- (4b) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.
- (4c) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673.
- (4d) Hanack, M.; Datz, A.; Fay, R.; Fischer, K.; Keppeler, U.; Koch, J.; Metz, J.; Mezger, M.; Schneider, O.; Schulze, H.-J. In "Handbook of Conducting Polymers"; Skotheim, T. A., Ed.; Dekker: New York, 1986; Vol. 2, pp. 133–204.
- (4e) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1980**, *41*, 149.
- (5) Myers, L. K.; Langhoff, C.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 7560; Fyfe, H. B.; Mlekuz, M.; Stringer, G.; Taylor, N. J.; Marder, T. B. In "Inorganic and Organometallic Polymers with Special Properties"; Laine, R. M., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; pp. 331–344; Porter, P. L.; Guha, S.; Kang, K.; Frazier, C. C. *Polymer* **1991**, *32*, 1756; Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245; Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. *ACS Symp. Ser.* **1991**, *455*, 605; Lesley, G.; Yuan, Z.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Koch, L.; Scott, K.; Marder, T. B.; Williams, I. D.; Kurtz, S. K. In "Organic Materials for Non-Linear Optics II"; Hann, R. A.; Bloor, D., Eds.; Royal Society of Chemistry: Cambridge, UK, 1991; pp. 197–203; Davey, A. P.; Cardin, D. J.; Byrne, H. J.; Blau, W. In "Organic

- Molecules for Nonlinear Optics and Photonics"; Messier, J.; Kajzar, F.; Prasad, P., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; pp. 391–402; Frazier, C. C.; Guha, S.; Chen, W. *PCT Int. Appl.* **1989**, *PCT Int. Appl. WO 89 01,182; Chem. Abstr.* **1989**, *111*, 105446p; Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, *14*, 952; Frazier, C. C.; Chauchard, E. A.; Cockerham, M. P.; Porter, P. L. *Mater. Res. Soc. Symp. Proc.* **1988**, *109*, 323; Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553.
- (6a) Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732.
- (6b) Dray, A. E.; Wittmann, F.; Friend, R. H.; Donald, A. M.; Khan, M. S.; Lewis, J.; Johnson, B. F. G. *Synth. Met.* **1991**, *41–43*, 871.
- (6c) Canadell, E.; Alvarez, S. *Inorg. Chem.* **1984**, *23*, 573.
- (6d) Seelig, F. F. Z. *Naturforsch., A* **1979**, *34A*, 986.
- (7a) Rourke, J. P.; Bruce, D. W.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **1995**, 317.
- (7b) Kaharu, T.; Matsubara, H.; Takahashi, S. *J. Mater. Chem.* **1992**, *2*, 43.
- (7c) Abe, A.; Kimura, N.; Tabata, S. *Macromolecules* **1991**, *24*, 6238.
- (7d) Kotani, S.; Shiina, K.; Sonogashira, K. *Appl. Organomet. Chem.* **1991**, *5*, 417.
- (7e) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1984**, 3.
- (7f) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K.; Hagihara, N. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 139.
- (8) Sharpe, A. G. In "Comprehensive Coordination Chemistry"; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2, pp. 7–14.
- (9) Wrackmeyer, B.; Horchler, K. *Prog. NMR Spectrosc.* **1990**, *22*, 209; Relevant papers since this review include
- (9a) Wrackmeyer, B.; von Locqueghien, K. H.; Kupče, E.; Sebal, A. *Magn. Reson. Chem.* **1993**, *31*, 45.
- (9b) Duer, M. J.; Khan, M. S.; Kakkar, A. K. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 13.
- (9c) Wrackmeyer, B. Z. *Naturforsch., B: Chem. Sci.* **1991**, *46B*, 35.
- (10) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.
- (11) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
- (12a) Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. *Organometallics* **1993**, *12*, 3522.
- (12b) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.
- (13) Louwen, J. N.; Hengelmolen, R.; Grove, D. M.; Oskam, A.; DeKock, R. L. *Organometallics* **1984**, *3*, 908.
- (14) Knight, E. T.; Myers, L. K.; Thompson, M. E. *Organometallics* **1992**, *11*, 3691.
- (15a) Stoner, T. C.; Schaefer, W. P.; Marsh, R. E.; Hopkins, M. D. *J. Clust. Sci.* **1994**, *5*, 107.
- (15b) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 409.
- (15c) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 4201.
- (15d) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651.
- (15e) John, K. D.; Hopkins, M. D. Unpublished results.
- (16a) Pollagi, T. P.; Manna, J.; Stoner, T. C.; Geib, S. J.; Hopkins, M. D. In "Transition Metal Carbyne Complexes"; Kreissl, F. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; pp. 71–73.

- (16b) Manna, J.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 9199.
- (16c) Manna, J.; Johnson, J. A.; Hopkins, M. D. Unpublished results.
- (17) Manna, J.; Geib, S. J.; Hopkins, M. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 858.
- (18) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2226.
- (19) Tahara, T.; Seto, K.; Takahashi, S. *Polym. J.* **1987**, *19*, 301; Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 565; Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *ibid.* **1980**, *18*, 661; Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *ibid.*, 349; Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319; Fujikura, Y.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1975**, 1067.
- (20a) Yam, V. W.-W.; Chan, L.-P.; Lai, T.-F. *Organometallics* **1993**, *12*, 2197.
- (20b) Sacksteder, L.; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 3955.
- (20c) Baralt, E.; Boudreaux, E. A.; Demas, J. N.; Lenhert, P. G.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Sacksteder, L.; True, W. R. *Organometallics* **1989**, *8*, 2417.
- (21) Sacksteder, L.; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 2468.
- (22) Yip, H.-K.; Lin, H.-M.; Wang, Y.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2939.
- (23) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165; Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Dray, A. E.; Friend, R. H.; Wittmann, F. *J. Mater. Chem.* **1991**, *1*, 485.
- (24) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.
- (25) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409; Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
- (26) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636; Rappé, A. K. *Organometallics* **1990**, *9*, 466.
- (27) Birchall, T.; Myers, R. D. *Spectrosc.: Int. J.* **1983**, *2*, 22.
- (28) Evans, D. J.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1785.
- (29) Sebald, A.; Wrackmeyer, B.; Beck, W. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 45.
- (30) Parshall, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 704.
- (31a) Köhler, F. H.; Prössdorf, W.; Schubert, U. *Inorg. Chem.* **1981**, *20*, 4096.
- (31b) Köhler, F. H.; Hofmann, P.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 6359.
- (31c) Köhler, F. H.; Prössdorf, W.; Schubert, U.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 850.
- (31d) Balch, A. L.; Latos-Grazyn'ski, L.; Noll, B. C.; Phillips, S. L. *Inorg. Chem.* **1993**, *32*, 1124.
- (32) Abu-Salah, O. M.; Al-Ohaly, A.-R. A.; Al-Showiman, S. S.; Al-Najjar, I. M. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 207.
- (33a) Bianchini, C.; Laschi, F.; Masi, D.; Ottaviani, F. M.; Pastor, A.; Peruzzini, M.; Zanello, P.; Zanobini, F. *J. Am. Chem. Soc.* **1993**, *115*, 2723.
- (33b) Bear, J. L.; Han, B.; Huang, S. *J. Am. Chem. Soc.* **1993**, *115*, 1175.



- (33c) Li, Y.; Han, B.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1993**, *32*, 4175.
- (33d) Connelly, N. G.; Gamasa, M. P.; Gimeno, J.; Lapinte, C.; Lastra, E.; Maher, J. P.; Le Narvor, N.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1993**, 2575; Correction: p. 2981.
- (33e) Field, L. D.; George, A. V.; Laschi, F.; Malouf, E. Y.; Zanello, P. *J. Organomet. Chem.* **1992**, *435*, 347.
- (33f) Hills, A.; Hughes, D. L.; Kashef, N.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1775.
- (33g) Beddoes, R. L.; Bitcon, C.; Whiteley, M. W. *J. Organomet. Chem.* **1991**, *402*, 85.
- (33h) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, F. M. *Organometallics* **1990**, *9*, 360.
- (33i) Yao, C. L.; Park, K. H.; Khokhar, A. R.; Jun, M.-J.; Bear, J. L. *Inorg. Chem.* **1990**, *29*, 4033.
- (33j) Bianchini, C.; Innocenti, P.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 2514.
- (33k) Bianchini, C.; Laschi, F.; Ottaviani, M. F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893.
- (33l) Hills, A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1988**, *350*, C4.
- (33m) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660.
- (33n) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1987**, 3049.
- (33o) Bitcon, C.; Whiteley, M. W. *J. Organomet. Chem.* **1987**, *336*, 385.
- (33p) Chakravarty, A. R.; Cotton, F. A. *Inorg. Chim. Acta* **1986**, *113*, 19.
- (34) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.
- (35) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund K.; Krüger, C. *Organometallics* **1989**, *8*, 911.
- (36) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Organomet. Chem.* **1992**, *428*, 13.
- (37) Wielstra Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, *8*, 2696.
- (38) Evans, W. J.; Bloom, I.; Doedens, R. J. *J. Organomet. Chem.* **1984**, *265*, 249.
- (39) Schubert, U.; Köhler, F. H.; Prössdorf, W. *Cryst. Struct. Commun.* **1981**, *10*, 245.
- (40) Buang, N. A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1987**, *323*, C47.
- (41) Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1990**, *398*, C15.
- (42) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *367*, C21.
- (43) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1157.
- (44) Sieber, W.; Wolfgruber, M.; Neugebauer, D.; Orama, O.; Kreissl, F. R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 67.
- (45) Valín, M. L.; Moreiras, D.; Solans, X.; Miguel, D.; Riera, V. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 977.
- (46) Grigsby, W. J.; Main, L.; Nicholson, B. K. *Organometallics* **1993**, *12*, 397.
- (47) Goldberg, S. Z.; Duesler, E. N.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 1397; *Chem. Commun.* **1971**, 826.
- (48) Cramer, R. E.; Higa, K. T.; Gilje, J. W. *Organometallics* **1985**, *4*, 1140.

- (49) Batsanov, A. S.; Struchkov, Y. T.; Zhdanovich, V. I.; Petrovskii, P. V.; Kolobova, N. E. *Metalloorg. Khim.* **1989**, 2, 1045.
- (50) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, 110, 6096.
- (51) Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, 107, 631.
- (52a) Field, L. D.; George, A. V.; Malouf, E. Y.; Slip, I. H. M.; Hambley, T. W. *Organometallics* **1991**, 10, 3842.
- (52b) Field, L. D.; George, A. V.; Hambley, T. W.; Malouf, E. Y.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 931.
- (53) Hughes, D. L.; Leigh, G. J.; Jimenez-Tenorio, M.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 75; Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Organomet. Chem.* **1990**, 391, C41.
- (54) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, 29, 4565.
- (55) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3151.
- (56) Löwe, C.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, 372, 295.
- (57) Goddard, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2025.
- (58) Gamasa, M. P.; Gimeno J.; Lastra, E. *J. Organomet. Chem.* **1991**, 405, 333.
- (59) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, 9, 816.
- (60) Kruger, G. J.; Ashworth, T. V.; Singleton, E. *Acta Crystallogr., Sect. A: Cryst. Phys., Differ., Theor. Geo., Crystallogr.* **1981**, A37, C220.
- (61) Atherton, Z.; Faulkner, C. W.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1993**, 462, 265.
- (62) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, 12, 3132; Haquette, P.; Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 163.
- (63a) Sun, Y.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1992**, 423, C43.
- (63b) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, 11, 4293.
- (64) Echavarren, A. M.; López, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, 10, 2371.
- (65) Montoya, J.; Santos, A.; López, J.; Echavarren, A. M.; Ros, J.; Romero, A. *J. Organomet. Chem.* **1992**, 426, 383.
- (66a) Jia, G.; Gallucci, J. C.; Rheingold, A. L.; Haggerty, B. S.; Meek, D. W. *Organometallics* **1991**, 10, 3459.
- (66b) Jia, G.; Rheingold, A. L.; Meek, D. W. *ibid.* **1989**, 8, 1378.
- (67) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, 6, 1091.
- (68) Helliwell, M.; Stell, K. M.; Mawby, R. J. *J. Organomet. Chem.* **1988**, 356, C32.
- (69) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, 100, 115.
- (70) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, 314, 213.
- (71) Lomprey, J. R.; Selegue, J. P. *Organometallics* **1993**, 12, 616.
- (72) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, 450, 209.
- (73) Consiglio, G.; Morandini, F.; Sironi, A. *J. Organomet. Chem.* **1986**, 306, C45.
- (74) Romero, A.; Peron, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1410.
- (75) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, 12, 36.
- (76) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, 12, 663.

- (77) Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 385.
- (78) Klein, H.-F.; Beck, H.; Hammerschmitt, B.; Koch, U.; Koppert, S.; Cordier, G. *Z. Naturforsch., B: Chem. Sci.* **1991**, 46B, 147.
- (79) Stringer, G.; Taylor, N. J.; Marder, T. B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* (accepted for publication).
- (80) Garcia Basallote, M.; Hughes, D. L.; Jiménez-Tenorio, M.; Leigh, G. J.; Puerta Vizcaino, M. C.; Valerga Jiménez, P. *J. Chem. Soc., Dalton Trans.* **1993**, 1841.
- (81) Giese, B.; Zehnder, M.; Neuburger, M.; Trach, F. *J. Organomet. Chem.* **1991**, 412, 415.
- (82) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanolini, F. *Organometallics* **1991**, 10, 3697.
- (83) Habadie, N.; Dartiguenave, M.; Dartiguenave, Y.; Britten, J. F.; Beauchamp, A. L. *Organometallics* **1989**, 8, 2564.
- (84) Kergoat, R.; Gomes de Lima, L. C.; Jégat, C.; Le Berre, N.; Kubicki, M. M.; Guerchais, J. E. *J. Organomet. Chem.* **1990**, 389, 71.
- (85) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540.
- (86a) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.
- (86b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Marder, T. B. In "Organic Materials for Non-Linear Optics II"; Hann, R. A.; Bloor, D., Eds.; Royal Society of Chemistry: Cambridge, UK, 1991; pp. 204–209.
- (87) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, 235, 105.
- (88a) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanolini, F. *Organometallics* **1989**, 8, 2179.
- (88b) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanolini, F. *J. Organomet. Chem.* **1988**, 346, C53.
- (89) Marder, T. B.; Zargarian, D.; Calabrese, J. C.; Herskovitz, T. H.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1484.
- (90) Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1545.
- (91) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, 13, 1089.
- (92) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, 11, 4156.
- (93) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. Apreda, M.-C.; Concepcion, F.-F.; Cano, F. H. *Organometallics* **1989**, 8, 1158.
- (94) Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Organometallics* **1983**, 2, 1889.
- (95) O'Connor, J. M.; Pu, L.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, 112, 9627.
- (96) Callahan, K. P.; Strouse, C. E.; Layten, S. W.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 465.
- (97) Davies, G. R.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc. A* **1967**, 1750.
- (98) Spofford, W. A., III; Carfagna, P. D.; Amma, E. L. *Inorg. Chem.* **1967**, 6, 1553.
- (99) von Deuten, K.; Beyer, A.; Nast, R. *Cryst. Struct. Commun.* **1979**, 8, 755.
- (100) van der Voort, E.; Spek, A. L.; de Graaf, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, C43, 2311.
- (101) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.

- (102) Yasuda, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2888.
- (103) Behrens, U.; Hoffmann, K. *J. Organomet. Chem.* **1977**, *129*, 273.
- (104) de Graaf, W.; Harder, S.; Boersma, J.; van Koten, G.; Kanters, J. A. *J. Organomet. Chem.* **1988**, *358*, 545.
- (105) Sünkel, K. *J. Organomet. Chem.* **1992**, *436*, 101.
- (106) Sebald, A.; Stader, C.; Wrackmeyer, B.; Bensch, W. *J. Organomet. Chem.* **1986**, *311*, 233.
- (107) Carpenter, J. P.; Lukehart, C. M. *Inorg. Chim. Acta* **1991**, *190*, 7.
- (108) Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C. *Cryst. Struct. Commun.* **1976**, *5*, 139.
- (109) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, *46*; *J. Organomet. Chem.* **1973**, *60*, C70.
- (110) Sünkel, K. *J. Organomet. Chem.* **1988**, *348*, C12.
- (111) Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C.; Carusi, P.; Furlani, A.; Russo, M. V. *Cryst. Struct. Commun.* **1977**, *6*, 623.
- (112) Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C.; Carusi, P.; Furlani, A.; Russo, M. V. *Cryst. Struct. Commun.* **1977**, *6*, 629.
- (113) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1984**, 2197.
- (114) Furlani, A.; Russo, M. V.; Licoccia, S.; Guastini, C. *Inorg. Chim. Acta* **1979**, *33*, L125.
- (115) Wouters, J. M. A.; Vrieze, K.; Elsevier, C. J.; Zoutberg, M. C.; Goubitz, K. *Organometallics* **1994**, *13*, 1510.
- (116) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2449.
- (117) Behrens, U.; Hoffmann, K.; Kopf, J.; Moritz, J. *J. Organomet. Chem.* **1976**, *117*, 91.
- (118) Kowalski, M. H.; Arif, A. M.; Stang, P. J. *Organometallics* **1988**, *7*, 1227.
- (119) Furlani, A.; Russo, M. V.; Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1977**, 2154.
- (120) Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C. *Cryst. Struct. Commun.* **1977**, *6*, 313.
- (121) Onuma, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1696.
- (122) Li, X.; Lukehart, C. M.; Han, L. *Organometallics* **1992**, *11*, 3993.
- (123) Croatto, U.; Toniolo, L.; Immirzi, A.; Bombieri, G. *J. Organomet. Chem.* **1975**, *102*, C31.
- (124) Phillips, J. R.; Miller, G. A.; Trogler, W. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1648.
- (125) Bonamico, M.; Dessy, G.; Fares, V.; Russo, M. V.; Scaramuzza, L. *Cryst. Struct. Commun.* **1977**, *6*, 39.
- (126) Kubota, M.; Sly, W. G.; Santarsiero, B. D.; Clifton, M. S.; Kuo, L. *Organometallics* **1987**, *6*, 1257.
- (127) Baddley, W. H.; Panattoni, C.; Bandoli, G.; Clemente, D. A.; Belluco, U. *J. Am. Chem. Soc.* **1971**, *93*, 5590.
- (128) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356.
- (129) Weigand, W.; Robl, C. *Chem. Ber.* **1993**, *126*, 1807.
- (130) Mariezcurrena, R. A.; Rasmussen, S. E. *Acta Chem. Scand.* **1973**, *27*, 2678.
- (131) Geisenberger, J.; Nagel, U.; Sebald, A.; Beck, W. *Chem. Ber.* **1983**, *116*, 911.
- (132a) Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 1815.

- (132b) Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, 76, L265.
- (133) Hutton, A. T.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2121.
- (134) Manojlović-Muir, L.; Henderson, A. N.; Treurnicht, I.; Puddephatt, R. J. *Organometallics* **1989**, 8, 2055.
- (135) Manojlović-Muir, L.; Muir, K. W.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1987**, 26, 2418; Arsenault, G. J.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Treurnicht, I. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 86.
- (136) Alcock, N. W.; Kemp, T. J.; Pringle, P. G.; Bergamini, P.; Traverso, O. *J. Chem. Soc., Dalton Trans.* **1987**, 1659.
- (137) DePriest, J. C.; Woods, C. *Polyhedron* **1991**, 10, 2153.
- (138) Markham, D. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1005.
- (139) Baralt, E.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *Organometallics* **1991**, 10, 516.
- (140) Lukehart, C. M.; Owen, M. D. *J. Clust. Sci.* **1991**, 2, 71.
- (141) Smith, D. E.; Welch, A. J.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1986**, 25, 4616.
- (142) McDonald, W. S.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 861.
- (143) Berenguer, J. R.; Fornies, J.; Lalinde, E.; Martinez, F.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1291.
- (144) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, 106, 3050.
- (145) Ciriano, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1979**, 1749.
- (146) Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, 39, 1697.
- (147) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1967**, 23, 156.
- (148) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, 37, 1163.
- (149) Carriedo, G. A.; Riera, V.; Solans, X.; Solans, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, C44, 978.
- (150) Jia, G.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, 12, 4771; Jia, G.; Puddephatt, R. J.; Vittal, J. J.; Payne, N. C. *ibid.*, 263.
- (151) Jia, G.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, 12, 3565.
- (152) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; p 176.
- (153) McMullan, R. K.; Kvik, Å.; Popelier, P. *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, B48, 726.
- (154) Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry"; Brooks-Cole: Monterey, CA, 1985; Chapter 2.
- (155) The decision to include in the distribution (Figure 2) all crystallographically distinct C≡C bond lengths (e.g., eight distances for Mo<sub>2</sub>(CCMe)<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>), rather than to either also double count crystallographically equivalent bond lengths (e.g., two distances of 1.206 Å for ZrCp<sub>2</sub>(CCMe)<sub>2</sub>) or to simply count the mean C≡C bond length for ML<sub>n</sub>(CCR)<sub>x</sub> (x > 1) complexes with chemically equivalent alkynyl ligands (e.g., 1.195 Å for Mo<sub>2</sub>(CCMe)<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>) was based on the presumption that the characteristics of the distribution have less to do with intrinsic chemical differences among compounds than they do with crystallographic differences. Even though different distributions are obtained under these alternate criteria, the mean C≡C bond length remains identical to that obtained by the method we adopted:

with double counting of crystallographically equivalent  $\text{C}\equiv\text{C}$  bond lengths,  $d(\text{C}\equiv\text{C})_{\text{mean}} = 1.201(17) \text{ \AA}$ ; counting only the mean  $\text{C}\equiv\text{C}$  bond length for each compound with more than one chemically equivalent ligand,  $d(\text{C}\equiv\text{C})_{\text{mean}} = 1.201(18) \text{ \AA}$ .

- (156) Fast, H.; Welsh, H. L. *J. Mol. Spectrosc.* **1972**, *41*, 203.
- (157) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
- (158) Botschwina, P. In "Ion and Cluster Ion Spectroscopy and Structure"; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; pp. 59–108.
- (159) Ervin, K. M.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 1167.
- (160) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper Collins: New York, 1993; pp. 182–199.
- (161) Pauling, L. "The Nature of the Chemical Bond"; Cornell Univ. Press: Ithaca, NY, 1960; Chapters 3 and 7.
- (162) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.
- (163) Wells, A. F. *J. Chem. Soc.* **1949**, 55; Pearson, R. G. *J. Chem. Soc., Chem. Commun.* **1968**, 65; Barbe, J. *J. Chem. Educ.* **1983**, *60*, 640; Peter, L. *ibid.* **1986**, *63*, 123.
- (164) Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926.
- (165) Porterfield, W. W. "Inorganic Chemistry: A Unified Approach"; Academic Press: San Diego; 1993; p. 215; Porterfield, W. W. Personal communication, 1994.
- (166) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34, 223.
- (167) Hunter, W. E.; Hrcir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.
- (168) Cotton, F. A.; Weisinger, K. J. *Inorg. Chem.* **1990**, *29*, 2594.
- (169) Ressler, J. M.; Wernett, P. C.; Kraihanzel, C. S.; Rheingold, A. L. *Organometallics* **1988**, *7*, 1661.
- (170) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Richardson, J. F. *Organometallics* **1990**, *9*, 424.
- (171) Stille, J. K.; Smith, C.; Anderson, O. P.; Miller, M. M. *Organometallics* **1989**, *8*, 1040.
- (172) Consiglio, G.; Morandini, F.; Ciani, G.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 333.
- (173) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc. Jpn.* **1985**, 586.
- (174) de Graaf, W.; Boersma, J.; Grove, D.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas.* **1988**, *107*, 299.
- (175) Bardi, R.; Piazzesi, A. M. *Inorg. Chim. Acta* **1981**, *47*, 249.
- (176) Ito, Y.; Inouye, M.; Sugimoto, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41.
- (177) The Pd—C bond length of  $\text{PdMeBr}(\text{NMe}_2\text{CH}_2\text{C}_6\text{H}_4\text{-2-PPh}_2)$  ( $2.142(8) \text{ \AA}$ , with methyl trans to the nitrogen atom), reported in the same paper as  $\text{Pd}(\text{C}\equiv\text{CSiMe}_3)\text{Br}(\text{NMe}_2\text{CH}_2\text{C}_6\text{H}_4\text{-2-PPh}_2)$  (104), would seem to be a perfect reference point, yielding  $\Delta d(\text{Pd}-\text{C}) = 0.20 \text{ \AA}$ . We have not used it for this purpose because it appears to be anomalously long, as seen by comparison to the Pd—C bond distances of  $\text{PdMe}_2(\text{tmeda})$  ( $2.028(3) \text{ \AA}$ ) (174) and *cis*- $\text{PdMe}_2(\text{PPh}_2\text{Me})_2$  ( $2.090(3) \text{ \AA}$ ; Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Organometallics* **1986**, *5*, 2044).
- (178) Morino, Y.; Kuchitsu, K.; Fukuyama, T.; Tanimoto, M. *Acta Crystallogr., Sect. A: Cryst. Phys., Differ., Theor. Gen. Crystallogr.* **1969**, *A25*, S127; Sugie, M.; Kuchitsu, K. *J. Mol. Struct.* **1974**, *20*, 437.
- (179) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739.

- (180) Staples, R. J.; Khan, M. N. I.; Wang, S.; Fackler, J. P., Jr. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, C48, 2213.
- (181) Jones, P. G.; Lautner, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, C44, 2091.
- (182) The *trans*-PtR<sub>2</sub>(PR')<sub>2</sub> (R = CN, alkynyl) comparison is valid, even though the pairs of alkynyl and cyano ligands in the two complexes do not share a common trans ligand, because the trans influences of the CN and CCR ligands are very similar (*vide infra*).
- (183) Cowie, J.; Hamilton, E. J. M.; Laurie, J. C. V.; Welch, A. J. *J. Organomet. Chem.* **1990**, 394, 1.
- (184) Williams, E. A. In "The Chemistry of Organic Silicon Compounds"; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Part I, Chapter 8; Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, 115, 11598.
- (185) Hartley, F. R. *Chem. Soc. Rev.* **1973**, 2, 163. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, 10, 335; Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, 18, 2112.
- (186a) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, 17, 738.
- (186b) Manojlović-Muir, L. J.; Muir, K. W. *Inorg. Chim. Acta* **1974**, 10, 47.
- (187) Bardi, R.; Piazzesi, A. M.; Cavinato, G.; Cavoli, P.; Toniolo, L. *J. Organomet. Chem.* **1982**, 224, 407.
- (188) Diré, S.; Campostrini, R.; Carturan, G.; Calligaris, M.; Nardin, G. *J. Organomet. Chem.* **1990**, 390, 267.
- (189) Bardi, R.; Piazzesi, A. M.; del Pra, A.; Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1982**, 234, 107.
- (190) Bennett, M. A.; Ho, K.-C.; Jeffery, J. C.; McLaughlin, G. M.; Robertson, G. B. *Aust. J. Chem.* **1982**, 35, 1311.
- (191) Graziani, R.; Cavinato, G.; Casellato, U.; Toniolo, L. *J. Organomet. Chem.* **1988**, 353, 125.
- (192) Kaduk, J. A.; Ibers, J. A. *J. Organomet. Chem.* **1977**, 139, 199.
- (193) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, 109, 148.
- (194) Wiege, M.; Brune, H. A.; Klein, H.-P.; Thewalt, U. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, 37B, 718.
- (195) Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, 18, 1061.
- (196) Conzelmann, W.; Koola, J. D.; Kunze, U.; Strähle, J. *Inorg. Chim. Acta* **1984**, 89, 147.
- (197) Solans, X.; Miravittles, C.; Arrieta, J. M.; Germain, G.; Declercq, J. P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, B38, 1812.
- (198) del Pra, A.; Zanotti, G.; Bombieri, G.; Ros, R. *Inorg. Chim. Acta* **1979**, 36, 121.
- (199) Davies, J. A.; Pinkerton, A. A.; Staples, R. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, C46, 48.
- (200) Phang, L.-T.; Au-Yeung, S. C. F.; Hor, T. S. A.; Khoo, S. B.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1993**, 165.
- (201) Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1987**, 26, 519.
- (202) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1980**, 192, 283.
- (203) Barron, P. F.; Engelhardt, L. M.; Healy, P. C.; Oddy, J.; White, A. H. *Aust. J. Chem.* **1987**, 40, 1545.
- (204) Åhrland, S.; Dreisch, K.; Norén, B.; Oskarsson, Å. *Acta Chem. Scand., Ser. A* **1987**, A41, 173.
- (205) Baenziger, N. C.; Bennett, W. E.; Soboroff, D. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, B32, 962.
- (206) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1981**, 20, 3430.

- (207) Grindley, T. B.; Johnson, K. F.; Katritzky, A. R.; Keogh, H. J.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 273; Grindley, T. B.; Johnson, K. F.; Katritzky, A. R.; Keogh, H. J.; Thirkettle, C.; Brownlee, R. T. C.; Munday, J. A.; Topsom, R. D. *ibid.*, 276; Grindley, T. B.; Johnson, K. F.; Katritzky, A. R.; Keogh, H. J.; Thirkettle, C.; Topsom, R. D. *ibid.*, 282. See also the references cited in these papers.
- (208a) Köpf, H.; Schmidt, M. *J. Organomet. Chem.* **1967**, 10, 383.
- (208b) Teuben, J. H.; de Liefde Mijer, H. J. *J. Organomet. Chem.* **1969**, 17, 87.
- (209a) Jimenez, R.; Barral, M. C.; Moreno, V.; Santos, A. *J. Organomet. Chem.* **1979**, 174, 281.
- (209b) Lang, H.; Seyferth, D. Z. *Naturforsch., B: Chem. Sci.* **1990**, 45B, 212.
- (210) Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Organomet. Chem.* **1970**, 23, 165.
- (211) Barral, M. C.; Jimenez, R.; Santos, A. *Inorg. Chim. Acta* **1982**, 63, 257.
- (212) Lang, H.; Seyferth, D. *Appl. Organomet. Chem.* **1990**, 4, 599.
- (213) Schlientz, W. J.; Ruff, J. K. *J. Chem. Soc. A* **1971**, 1139.
- (214) Nast, R.; Köhl, H. Z. *Anorg. Allg. Chem.* **1963**, 320, 135.
- (215) Taube, R.; Dreves, H.; Marx, G. Z. *Anorg. Allg. Chem.* **1977**, 436, 5.
- (216) Nesmeyanov, A. N.; Makarova, L. G.; Vinogradova, V. N.; Korneva, V. N.; Ustynyuk, N. A. *J. Organomet. Chem.* **1979**, 166, 217.
- (217) Nast, R.; Köhl, H. *Chem. Ber.* **1964**, 97, 207.
- (218) Villemin, D.; Schigeko, E. *J. Organomet. Chem.* **1988**, 346, C24.
- (219) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, 12, 404.
- (220) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.
- (221) Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1985**, 4, 2062.
- (222) Bruce, M. I.; Humphrey, M. G.; Matison, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, 37, 1955.
- (223) Eberl, K.; Uedelhoven, W.; Wolfgruber, M.; Kreissl, F. R. *Chem. Ber.* **1982**, 115, 504.
- (224) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, 114, 2951.
- (225) Nast R., Müller, H.-P. *Chem. Ber.* **1978**, 111, 415.
- (226) Ustynyuk, N. A.; Vinogradova, V. N.; Petrovskii, P. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 680.
- (227a) Carriedo, G. A.; Riera, V.; Miguel, D.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Organomet. Chem.* **1984**, 272, C17.
- (227b) Miguel, D.; Riera, V. *J. Organomet. Chem.* **1985**, 293, 379.
- (228) Bruce, M. I.; Harbourne, D. A.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 356.
- (229) Carvalho, M. F. N. N.; Herrmann, R.; Pombeiro, A. J. L. *Monatsh. Chem.* **1993**, 124, 739.
- (230) Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J. *J. Organomet. Chem.* **1991**, 409, C12.
- (231) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Raithby, P. R.; Fuhrmann, K.; Friend, R. H. *J. Organomet. Chem.* **1992**, 433, 135.
- (232) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, 100, 7577.
- (233) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, 118, 65.
- (234) Nast, R.; Krüger, K. W.; Beck, G. Z. *Anorg. Allg. Chem.* **1967**, 350, 177.
- (235) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, 11, 138; Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediani, P. *ibid.* **1989**, 8, 2080.
- (236) Hanack, M.; Knecht, S.; Schulze, H.-J. *J. Organomet. Chem.* **1993**, 445, 157.
- (237) Taube, R.; Dreves, H. Z. *Anorg. Allg. Chem.* **1977**, 429, 5.



- (238) Steinborn, D.; Sedlak, U.; Dargatz, M. *J. Organomet. Chem.* **1991**, *415*, 407.
- (239) Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99.
- (240) Davies, S. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1991**, *414*, C51.
- (241) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187.
- (242) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.
- (243) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.
- (244) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988.
- (245) Santos, A.; López, J.; Matas, L.; Ros, J.; Galán, A.; Echavarren, A. M. *Organometallics* **1993**, *12*, 4215.
- (246) Critchlow, P. B.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 1902.
- (247) Kohlmann, W.; Werner, H. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48B*, 1499.
- (248) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444.
- (249) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837.
- (250) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.
- (251a) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 82.
- (251b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471.
- (252) Abu Salah, O. M.; Bruce, M. I. *J. Chem. Soc., Dalton Trans.* **1975**, 2311.
- (253) Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *359*, 379.
- (254) Bruce, M. I.; Humphrey, M. G. *Aust. J. Chem.* **1989**, *42*, 1067.
- (255) Sato, M.; Sekino, M. *J. Organomet. Chem.* **1993**, *444*, 185.
- (256) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797.
- (257) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768.
- (258) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1.
- (259) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471.
- (260) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.
- (261) Knaup, W.; Werner, H. *J. Organomet. Chem.* **1991**, *411*, 471.
- (262) Werner, H.; Weinand, R.; Knaup, W.; Peters, K.; von Schnering, H. G. *Organometallics* **1991**, *10*, 3967; Weinand, R.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1145.
- (263) Nast, R.; Fock, K. *Chem. Ber.* **1976**, *109*, 455.
- (264) Nast, R.; Fock, K. *Chem. Ber.* **1977**, *110*, 280.
- (265) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944.
- (266) van den Bergen, A. M.; Elliott, R. L.; Lyons, C. J.; MacKinnon, K. P.; West, B. O. *J. Organomet. Chem.* **1985**, *297*, 361.
- (267) Mestroni, G.; Zassinovich, G.; Camus, A.; Costa, G. *J. Organomet. Chem.* **1975**, *92*, C35.
- (268) Khan, M. S.; Pasha, N. A.; Kakkar, A. K.; Raithby, P. R.; Lewis, J.; Fuhrmann, K.; Friend, R. H. *J. Mater. Chem.* **1992**, *2*, 759.
- (269) Werner, H.; Schneider, D.; Schulz, M. *J. Organomet. Chem.* **1993**, *451*, 175.
- (270) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397.
- (271) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1990**, *381*, 275.

- (272a) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202.
- (272b) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. *J. Organomet. Chem.* **1972**, 34, C37.
- (273) Schäfer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341.
- (274) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, 424, 87; Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187.
- (275) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 414.
- (276) Stang, P. J.; Crittall, C. M. *Organometallics* **1990**, 9, 3191.
- (277) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1987**, 971.
- (278) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, 9, 241.
- (279) Brekau, U.; Werner, H. *Organometallics* **1990**, 9, 1067.
- (280) Werner, H.; Höhn, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, 39B, 1505.
- (281) Nast, R.; Dahlenburg, L. *Chem. Ber.* **1972**, 105, 1456.
- (282a) Walter, R. H.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1978**, 381.
- (282b) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1370.
- (283) Werner, H.; Höhn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777.
- (284) Burgess, J.; Howden, M. E.; Kemmitt, R. D. W.; Sridhara, N. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1577.
- (285) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, 12, 2505.
- (286a) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, 382, 255.
- (286b) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 406.
- (286c) Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, 272, 105.
- (287) Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* **1977**, 30, 1213.
- (288) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, 89, 844.
- (289) Ballester, L.; Cano, M.; Santos, A. *J. Organomet. Chem.* **1982**, 229, 101.
- (290) Masai, H.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1971**, 26, 271.
- (291) Carusi, P.; Furlani, A. *Gazz. Chim. Ital.* **1980**, 110, 7.
- (292) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 1718.
- (293) Oguro, K.; Wada, M.; Okawara, R. *J. Organomet. Chem.* **1978**, 159, 417.
- (294) Wada, M.; Oguro, K.; Kawasaki, Y. *J. Organomet. Chem.* **1979**, 178, 261.
- (295) Seidel, W.; Genitz, D. Z. *Chem.* **1979**, 19, 413.
- (296) Fontaine, X. L. R.; Higgins, S. J.; Langrick, C. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1987**, 777.
- (297) Yamazaki, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1964**, 37, 907.
- (298) Yamazaki, H.; Nishido, T.; Matsumoto, Y.; Sumida, S.; Hagihara, N. *J. Organomet. Chem.* **1966**, 6, 86.
- (299) Nelson, J. H.; Verstuyft, A. W.; Kelly, J. D.; Jonassen, H. B. *Inorg. Chem.* **1974**, 13, 27.
- (300) Klein, H.-F.; Zettel, B.; Flörke, U.; Haupt, H.-J. *Chem. Ber.* **1992**, 125, 9.
- (301) Kim, Y.-J.; Osakada, K.; Yamamoto, A. *J. Organomet. Chem.* **1993**, 452, 247.
- (302) Espinet, P.; Forníés, J.; Martínez, F.; Sotes, M.; Lalinde, E.; Moreno, M. T.; Ruiz, A.; Welch, A. J. *J. Organomet. Chem.* **1991**, 403, 253.

- (303) Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1976**, *110*, C53.
- (304) Nast, R.; Müller, H.-P.; Pank, V. *Chem. Ber.* **1978**, *111*, 1627.
- (305) Perera, S. D.; Shaw, B. L. *J. Organomet. Chem.* **1991**, *402*, 133.
- (306) Nast, R.; Heinz, W.-D. *Chem. Ber.* **1962**, *95*, 1478.
- (307) Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2487.
- (308) Nast, R.; Voss, J.; Kramolowsky, R. *Chem. Ber.* **1975**, *108*, 1511.
- (309) Forniés, J.; Gómez-Saso, M. A.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1992**, *11*, 2873.
- (310) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101.
- (311) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 4020.
- (312) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1967**, 1066.
- (313) Yamazaki, S. *Polyhedron* **1992**, *11*, 1983.
- (314) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051.
- (315) Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. *Inorg. Chem.* **1977**, *16*, 677.
- (316) Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *209*, 415.
- (317a) Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* **1976**, *29*, 73.
- (317b) Collamati, I.; Furlani, A. *J. Organomet. Chem.* **1969**, *17*, 457.
- (318) Russo, M. V.; Furlani, A. *J. Organomet. Chem.* **1979**, *165*, 101.
- (319) Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5359.
- (320) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 767.
- (321) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987.
- (322) Anderson, G. K.; Lumetta, G. J. *J. Organomet. Chem.* **1985**, *295*, 257.
- (323) Cook, C. D.; Jauhal, G. S. *Can. J. Chem.* **1967**, *45*, 301.
- (324) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *210*, 403.
- (325) Berenguer, J. R.; Forniés, J.; Martínez, F.; Cubero, J. C.; Lalinde, E.; Moreno, M. T.; Welch, A. J. *Polyhedron* **1993**, *12*, 1797.
- (326) Chisholm, M. H.; Clark, H. C. *Chem. Commun.* **1970**, 763.
- (327) Schenk, W. A.; Hilpert, G. H. *J. Chem. Ber.* **1991**, *124*, 433.
- (328) McEwan, D. M.; Markham, D. P.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1986**, 1809.
- (329) Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1015.
- (330) Cooper, G. R.; Hutton, A. T.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 855.
- (331) Abu-Salah, O. M.; Al-Ohaly, A. R. *J. Organomet. Chem.* **1983**, *255*, C39.
- (332) Nast, R.; Schneller, P.; Hengefeld, A. *J. Organomet. Chem.* **1981**, *214*, 273.
- (333) Nast, R.; Kirner, U. *Z. Anorg. Allg. Chem.* **1964**, *330*, 311.
- (334) Werner, H.; Otto, H.; Ngo-Khac, T.; Burschka, C. *J. Organomet. Chem.* **1984**, *262*, 123.
- (335) Bailey, J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1921.
- (336) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.
- (337) Nast, R.; Gremm, J. *Z. Anorg. Allg. Chem.* **1963**, *325*, 62.
- (338) Weiss, E.; Plass, H. *Chem. Ber.* **1968**, *101*, 2947.
- (339) Klein, H.-F.; Beck-Hemetsberger, H.; Reitzel, L.; Rodenhäuser, B.; Cordier, G. *Chem. Ber.* **1989**, *122*, 43; Barral, M. C.; Jimenez, R.; Royer, E.; Moreno, V.; Santos, A. *Inorg. Chim. Acta* **1978**, *31*, 165.
- (340) Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 687.

# Organotransition-Metal Chemistry and Homogeneous Catalysis in Aqueous Solution

D. M. ROUNDHILL

*Department of Chemistry  
Tulane University  
New Orleans, Louisiana*

I.	Introduction . . . . .	155
II.	Metal Alkyls . . . . .	156
	A. Alkylchromium(III) Complexes . . . . .	156
	B. Alkylcobalt(III) Complexes . . . . .	160
	C. Alkylplatinum(III) Complexes . . . . .	162
	D. Metal-Carbonyl Complexes . . . . .	163
III.	Tertiary Phosphines . . . . .	164
	A. Synthesis . . . . .	164
	B. Metal Complexes . . . . .	166
IV.	Homogeneous Catalysis . . . . .	167
	A. Transition-Metal Halides in Catalysis . . . . .	167
	B. Wacker Oxidation of Alkenes . . . . .	171
	C. Cobalt-Cyanide Complexes as Alkene Hydrogenation Catalysts . . . . .	171
	D. Tertiary Phosphine Complexes in Catalytic Hydroformylation and Hydrogenation Reactions . . . . .	172
	E. Asymmetric Catalysis with Tertiary Phosphine Complexes . . . . .	179
	F. Supramolecular-Medium Effects in Catalytic Reactions . . . . .	181
	G. Other Catalyzed Reactions . . . . .	182
	References . . . . .	184

## I

## INTRODUCTION

Although it is generally perceived that organometallic complexes are only stable in the absence of water, there is a growing interest in the use of water as both a reagent and a solvent for reactions involving such compounds. Whereas in some cases it is clear that this solvent acts destructively on organometallic complexes, there are other cases where the complexes are stable. For transition metals, the organometallic compound methylcobalamin has long been known to be stable in an aqueous environment (1), and for the main group elements both methylmercury and methyllead compounds are stable (2). In general for transition-metal systems, water-soluble organometallics are known for the kinetically inert metal ions.

More recently there has been a strong growth of interest in the use of transition metals as homogeneous catalysts in aqueous solution. These processes involve the intermediacy of organometallic compounds for cases where the catalysts are simple transition-metal halide salts or where the metal complexes contain water-soluble tertiary phosphines as ligands (3,4).

Water as a solvent offers a number of variations to those offered by organic solvents. Because of its high dielectric constant and its ability to hydrate strongly both cations and anions, it is a solvent that strongly favors ionic reactions. Structurally, water has only O-H bonds. The enthalpy of this bond is  $436 \text{ kJ mol}^{-1}$ , which is a very high value for a single bond. A consequence of this high bond enthalpy is that water is an excellent solvent for carrying out free-radical reactions because in order for a radical to abstract a hydrogen atom from water, the bond enthalpy of the bond formed between the new heteroatom and hydrogen must be greater than that of the O-H bond.

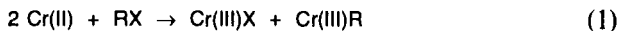
In this review we consider both the organometallic compounds that can be obtained in aqueous solution and the catalytic systems that can be used in this solvent. An attempt is made to correlate the two topics such that parallels can be drawn between the reactions that are observed in aqueous solution and the catalytic processes that can be used.

## II

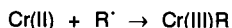
### METAL ALKYLs

#### A. Alkylchromium(III) Complexes

A series of alkylchromium(III) complexes have been prepared in aqueous solution. These complexes can be synthesized by reaction of the chromium(II) precursor with alkyl halides (Eq. 1) or alkyl radicals (Eq. 2) (5,6). Both of these schematic routes have been used to synthesize the

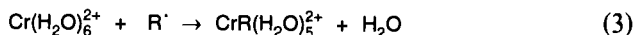


alkyl complexes  $\text{CrR(H}_2\text{O)}_5^{2+}$ . In the first case, with RX, the reaction sequence is a stepwise one, where the initial step involves halogen atom abstraction from the alkyl halide, followed by the trapping of the alkyl radical by a second molecule of the chromium(II) complex (Scheme I). The formation of alkyl complexes  $\text{CrR(H}_2\text{O)}_5^{2+}$  by trapping of the chromium(II)

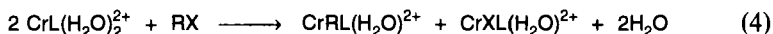


SCHEME 1.

hexaquo complex (Eq. 3) with alkyl radicals occurs for a wide range of R-groups. The complexes  $\text{CrR}(\text{H}_2\text{O})_5^{2+}$  are identified by absorption bands at 390–405 nm ( $\epsilon = 200\text{--}400 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 270–290 nm ( $\epsilon = 2\text{--}4 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 520–570 nm ( $\epsilon = 10\text{--}40 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The log of the



rate constant ( $\text{L mol}^{-1} \text{ sec}^{-1}$ ) for the different R-groups covers the range between 7.5 and 8.2 (6). The reaction shows a small positive volume of activation, which supports a pathway where chromium–carbon sigma-bond formation is controlled by solvent exchange on  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ . The reaction therefore follows an  $I_d$  mechanism (7). Macrocyclic Cr(II) complexes  $\text{CrL}(\text{H}_2\text{O})_2^{2+}$  ( $\text{L} = [14]\text{aneN}_4$ ) (Fig. 1) undergo similar reactions with alkyl halides RX to give  $\text{CrXL}(\text{H}_2\text{O})_2^{2+}$  and  $\text{CrRL}(\text{H}_2\text{O})_2^{2+}$  (Eq. 4).



Although there is a linear correlation between the reduction potentials of RX and the rate constants for their reaction with  $\text{CrL}(\text{H}_2\text{O})_2^{2+}$ , the pathway involves atom transfer and not electron transfer (8). An electron transfer pathway initially to give  $\text{X}^-$  and a kinetically inert Cr(III) complex would not result in subsequent substitution to give the product  $\text{CrXL}(\text{H}_2\text{O})_2^{2+}$ .

The alkyl complexes  $\text{CrR}(\text{H}_2\text{O})_5^{2+}$  undergo substitution reactions with either neutral ligands L or anions  $\text{X}^-$ . For the case of ethylenediamine as a neutral ligand, substitution leads to the formation of the complex  $\text{CrR}(\text{en})_2^{2+}$  (Eq. 5) (9). For the case of the thiocyanate ion, substitution

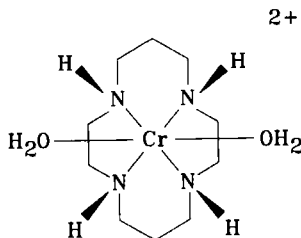
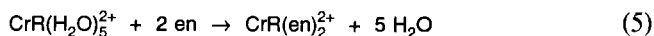
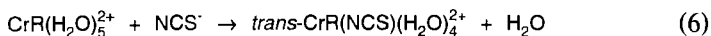


FIG. 1.

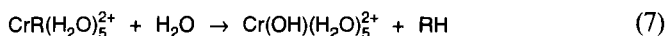


gives the complex *trans*-CrR(NCS)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> (Eq. 6) (10). The complexes CrR(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> generally decompose by the reverse of reaction 3. Since the high strength of the Cr–R bond frequently leads to this homolysis being



thermodynamically unfavorable, the reaction may occur only upon the addition of radical scavengers. The rates for this homolysis reaction are dependent on the nature of the R-group, with aralkyl and secondary alkyl derivatives being the most reactive. The primary alkyl complexes do not undergo significant homolysis. For the homolysis of the benzyl derivatives Cr(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X-4)(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup>, the reaction rate is lower when the substituent X is an electron-withdrawing group (11). Pulse radiolysis has been used effectively to determine the equilibrium constants for the homolytic cleavage of metal–carbon bonds. This kinetic method gives ΔH<sup>‡</sup> for the homolysis reaction. Taking this value as being a measure of the metal–carbon bond enthalpy, however, assumes that the radical recombination occurs at a rate close to the diffusion-controlled limit and has a negligible activation energy (12–14). The equilibrium constants for the Cr–R bond homolysis in CrR(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> for different R-groups are given in Table 1. These values for K do not correlate either with the redox potential of the group R or with the activation energy for the homolytic cleavage of the corresponding substituted ethanes.

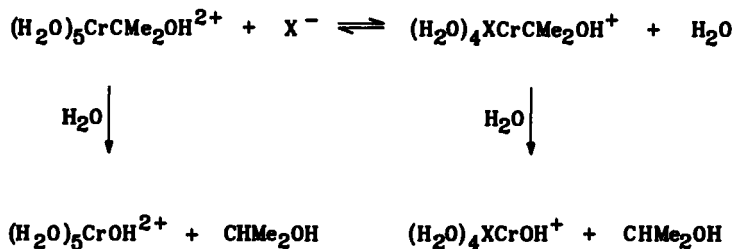
The complexes CrR(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> can also decompose by a heterolytic pathway (Eq. 7). The reaction rate for this pathway has terms that are both



first-order and independent of [H<sup>+</sup>]. In addition, the less-reactive alkyl complexes have heterolysis pathways that involve catalysis by sulfate

TABLE I  
EQUILIBRIUM CONSTANTS FOR THE Cr–R  
HOMOLYSIS IN CrR(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup>

R	K (mol dm <sup>-3</sup> )
CH <sub>2</sub> OH	2.3 × 10 <sup>-13</sup>
CH(Me)OH	1.1 × 10 <sup>-11</sup>
C(Me) <sub>2</sub> OH	2.5 × 10 <sup>-9</sup>
CH(Me)OEt	5.9 × 10 <sup>-11</sup>

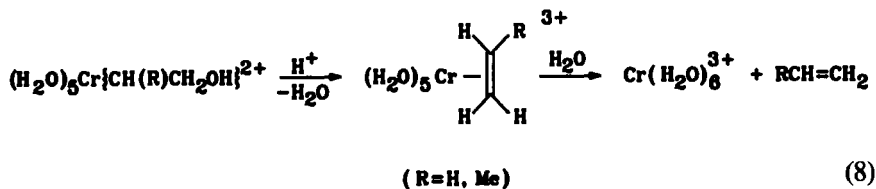


SCHEME 2.

ion. The uncatalyzed heterolysis pathway for a range of alkyl groups have  $\Delta H^\ddagger = 21 \pm 2 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -13.5 \pm 5 \text{ cal mol}^{-1} \text{ K}^{-1}$  (15). Acetate and similar anions catalyze this heterolysis reaction by *trans* labilization of the Cr–R bond (16–18). The presence of acetate ion also decreases the rate of reaction between  $\text{Cr}(\text{H}_2\text{O})_5^{2+}$  and alkyl radicals (R) to give alkylchromium(III) complexes  $\text{CrR}(\text{H}_2\text{O})_5^{2+}$ . This decrease corresponds with the reactive monomeric chromium(II) aquo complexes being converted by acetate ion into higher aggregates. Under high pressure, dissociation to monomers occurs and the reaction rate with alkyl radicals increases correspondingly (19). The heterolysis reaction can, however, become more dominant by the addition of aqueous chromium(II), which suppresses the homolysis of the Cr–R bond.

For the anion-catalyzed heterolysis reaction with the complex  $(\text{H}_2\text{O})_5\text{Cr}(\text{CMe}_2\text{OH})^{2+}$ , the catalytic effect increases with basicity of the anion. The activation volumes are all positive, in support of a dissociatively activated heterolysis mechanism. Overall, the decomposition mechanism involves parallel pathways whereby hydrolytic cleavage occurs at both  $(\text{H}_2\text{O})_5\text{Cr}(\text{CMe}_2\text{OH})^{2+}$  and the more-reactive substituted complex  $(\text{H}_2\text{O})_4\text{XCr}(\text{CMe}_2\text{OH})^+$  (Scheme 2).

Alkylchromium(III) complexes having alkyl groups that contain  $\beta$ -hydrogen and hydroxyl groups can decompose by an acid-catalyzed  $\beta$ -hydrogen transfer pathway. For the complex  $(\text{H}_2\text{O})_5\text{Cr}[\text{CH}(\text{R})\text{CH}_2\text{OH}]^{2+}$  (R = H, Me) in acidic solution, the decomposition products are  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and the alkene  $\text{RCH}=\text{CH}_2$ , which are formed via the  $\pi$ -bonded alkene complex (Eq. 8) (20). The replacement of a hydrogen substituent by a methyl



(8)

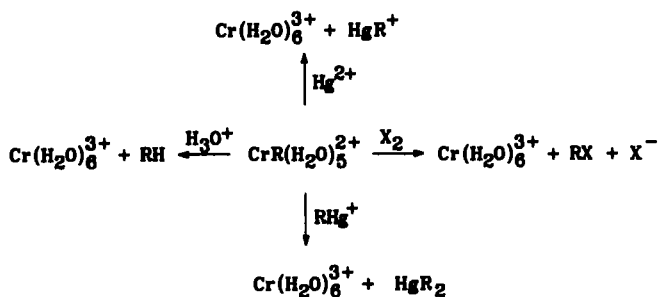


group results in a decrease in the rate of this reaction. Since similar studies on alkyl-copper and -cobalt complexes lead to different effects (21,22); therefore the origin of this retardation effect in the reaction rate is uncertain.

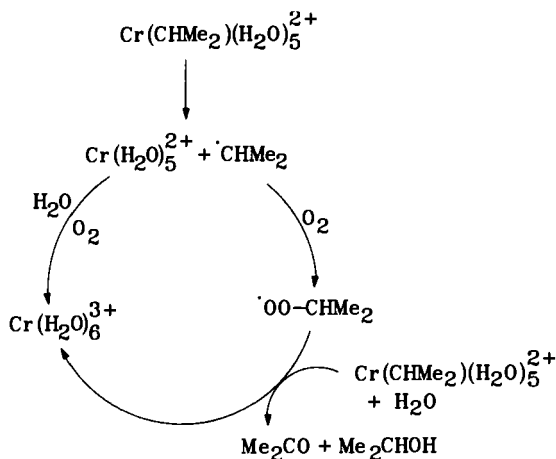
Organochromium complexes undergo a series of chemical reactions with electrophiles that result in cleavage of the Cr-R bond. The examples of such reactions shown in Scheme 3 result in transfer of the alkyl group to the electrophile and formation of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . The protonation reaction to give RH is slower than that with halogens or mercuric ions (23). These organochromium(III) complexes also react with other radicals, such as molecular oxygen. The reaction with oxygen follows a chain mechanism. In the mechanism shown for this reaction in Scheme 4 with the 2-propyl complex  $\text{Cr}(\text{CHMe}_2)(\text{H}_2\text{O})_5^{2+}$ , the oxygen molecule acts to trap any free 2-propyl radicals and convert them into hydroperoxyl radicals (24). Subsequent reaction of these hydroperoxyl radicals with  $\text{Cr}(\text{CHMe}_2)(\text{H}_2\text{O})_5^{2+}$  gives  $\text{Cr}(\text{OOCHMe}_2)(\text{H}_2\text{O})_5^{2+}$  and 2-propyl radicals. The final organic products are 2-propanol and acetone, with the radicals  $\bullet\text{CHMe}_2$  and  $\bullet\text{OO}-\text{CHMe}_2$  being the chain-carrying intermediates. The inorganic product is  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , which is formed from the reaction of  $\text{Cr}(\text{H}_2\text{O})_5^{2+}$  with oxygen in water.

### B. Alkylcobalt(III) Complexes

Alkylcobalt(III) complexes can also be synthesized in aqueous solution. Two of the best-known systems are methylcobalamin and a group of related cobaloximes, and alkylcobalt(III) complexes having ancillary cyanide ligands. As with the chromium(III) system, alkyl cobalt(III) complexes having dimethylglyoxime (DMG) or cyanide ligands can be synthesized by reaction of the cobalt(II) precursor with alkyl halides (Scheme



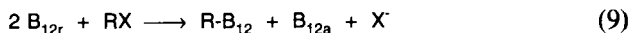
SCHEME 3.



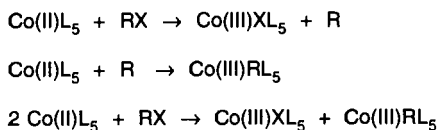
SCHEME 4.

5) (25). The reaction of the cobalt(II) complex  $\text{Co}(\text{CN})_5^{3-}$  with  $\text{RX}$  follows second-order kinetics, with the rate decreasing in the sequence  $\text{RI} > \text{RBr} \gg \text{RCl}$ . This sequence correlates with the bond enthalpies of the alkyl halides. The free-radical pathway for the reaction of  $\text{Co}(\text{CN})_5^{3-}$  with alkyl halides is shown in Scheme 6. The first step in Scheme 6 is the slow step; the second step is the fast one. For alkyl iodides the reaction rates follow the sequence  $\text{PhCH}_2\text{I} < \text{Me}_3\text{CI} > \text{Me}_2\text{CHI} > \text{EtI} > \text{MeI}$ . Again, this ordering corresponds with the highest rates being observed for compounds having the weakest carbon–iodine bond enthalpies (25).

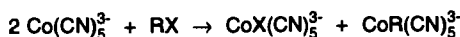
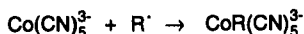
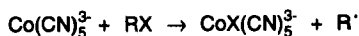
Alkylcobalt(III) cobalamin-type complexes can be prepared in aqueous solution by reaction between the reduced vitamin  $\text{B}_{12r}$  and organic halides (Eq. 9) (26,27). The reaction of vitamin  $\text{B}_{12r}$  with organic iodides in aqueous



solution, while exhibiting the same stoichiometry as in methanol, shows different kinetic behavior. In methanol as solvent, a second-order rate



SCHEME 5.



SCHEME 6.

law (Eq. 10) is observed; in aqueous solution, a third-order rate law (Eq. 11) is found. This third-order rate law has been explained on the basis of

$$-d[\text{B}_{12r}]/dt = 2k[\text{B}_{12r}][\text{RX}] \quad (10)$$

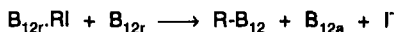
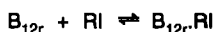
$$-d[\text{B}_{12r}]/dt = 2k[\text{B}_{12r}]^2[\text{RX}] \quad (11)$$

the mechanism shown in Scheme 7. This pathway involves a pre-equilibrium step where the initially formed adduct  $\text{B}_{12r}\text{RI}$  reacts with a second molecule of  $\text{B}_{12r}$  to give the observed products.

Pulse radiolysis has been used to study the transient formation and decomposition of cobalt-alkyl bonds in aqueous solution in the same manner as it has been used for chromium alkyls. And as for chromium alkyls, bond homolysis is a major decomposition pathway (28). For bond formation reactions, pulse radiolysis shows that they are assisted by increases in pressure. This feature results from the homolysis having a larger activation volume than the bond formation reaction, resulting in a significantly negative overall reaction volume for the process (29). In general for all of these metal-alkyl bond homolysis reactions of the aquo complexes, steric hindrance facilitates the reaction. Ligand effects also play a role, but the factors involved are more subtle.

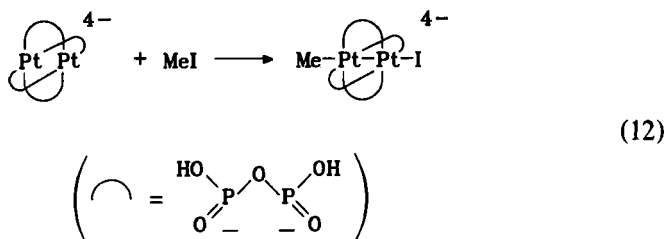
### C. Alkylplatinum(III) Complexes

Stable water-soluble alkylbisplatinum(III) complexes are known where the bridging ligand is a pyrophosphite. The iodomethyl diplatinum(III) complex has been prepared by the addition of methyl iodide to the tetrakis

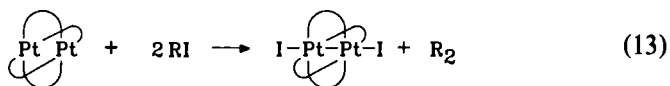


SCHEME 7.

( $\mu$ -pyrophosphito- $P,P'$ -)diplatinum(II) tetraanion  $\text{Pt}_2(\text{pop})_4^{4-}$  (Eq. 12).



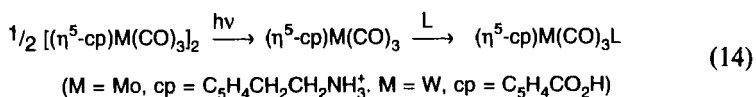
This reaction can even be carried out in strongly acidic solution, since the iodomethyl complex is stable in such conditions. No evidence is found for protolysis of the platinum–methyl bond. For higher-homolog alkyl groups, the stability of the iodoalkyl complex is lower, and the reaction of  $\text{Pt}_2(\text{pop})_4^{4-}$  with higher alkyl iodides may give the diiodo diplatinum(III) complex rather than the iodoalkyl complex (Eq. 13). These reactions



resemble the reaction of  $\text{Co}(\text{CN})_5^{3-}$  with alkyl halides, where a one-electron oxidation occurs at each metal center (30).

#### D. Metal–Carbonyl Complexes

Hydrophilic functional groups have been attached to cyclopentadienyl groups, and these compounds used as  $\eta^5$ -ligands toward transition-metal carbonyls. Two complexes that have been prepared with such ligands are  $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})\text{W}(\text{CO})_3]_2$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_3^+)\text{Mo}(\text{CO})_3]_2$  (31,32). Photolysis of these complexes in aqueous solution in the presence of added ligands L results in photodisproportionation of the complex and formation of 19-electron complexes  $(\eta^5\text{-cp})\text{M}(\text{CO})_3\text{L}$  ( $\text{M} = \text{Mo}$ ,  $\text{cp} = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_3^+$ ;  $\text{M} = \text{W}$ ,  $\text{cp} = \text{C}_5\text{H}_4\text{CO}_2\text{H}$ ) (Eq. 14). These complexes act as reductants to  $\text{Fe}(\text{CN})_6^{3-}$ , methyl viologen, and cytochrome c.



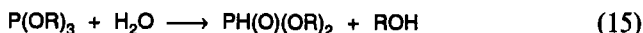
Metal–carbonyl complexes of the sodium salt of trisulfonated triphenylphosphine TPPTS (Section III-A) have also been synthesized. The prepar-

ative route involves photolysis of  $M(CO)_6$  ( $M = Mo, W$ ) with TPPTS in a coordinating solvent such as methanol (33). The complexes are stable, with the thermodynamics for TPPTS dissociation being comparable with  $PPh_3$  in nonaqueous solvents. The dissociation of TPPTS can, however, be accelerated by encapsulating the sodium ion of the ligand in a cryptand (34).

### III

#### TERTIARY PHOSPHINES

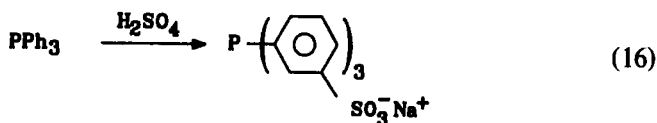
Since many organometallic compounds are stabilized by tertiary phosphines and phosphites, then if organometallic chemistry is to find major applications in aqueous solution it is necessary that these complexes be made compatible with such a solvent system. Water-soluble phosphines can be prepared by incorporating sulfonate or phosphonate groups into the molecule. Phosphites, however, are not a particularly good choice of ligand for reactions to be carried out in aqueous solution because they undergo hydrolysis to give phosphonites (Eq. 15). The coordination and



organometallic chemistry of phosphinites has been reviewed elsewhere (35,36), as has the use of tertiary phosphine complexes in aqueous solution as homogeneous catalysts (37–39).

##### A. Synthesis

A group of water-soluble tertiary phosphines that can be used as ligands to synthesize organometallic complexes soluble in aqueous solution are shown in Fig. 2. These individual phosphines can be synthesized by the sulfonation of triphenylphosphine, **1** (Eq. 16) (40); the reaction between



lithium diphenylphosphide and 2-chloroethyldimethylamine, **2** (Eq. 17) (41); the reaction between diphenylphosphide and sodium 2-bromoethyl-sulfonate, **3** (Eq. 18), or 2-bromoethyl-diethyl phosphonate, **4** (Eq. 19)

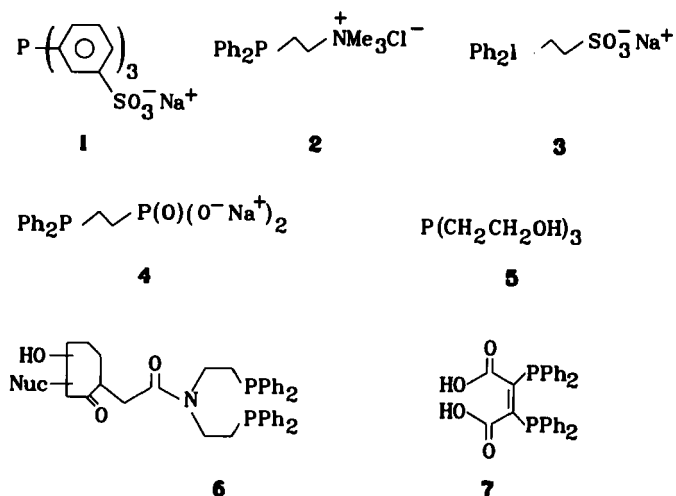
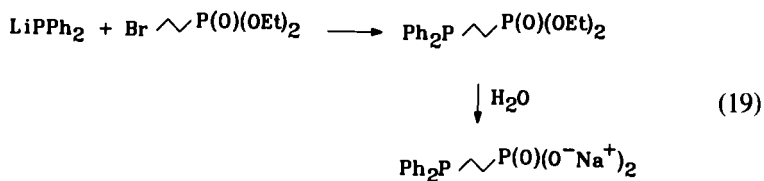
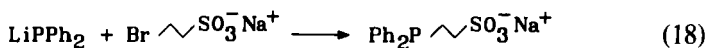
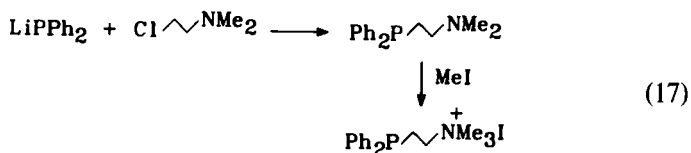
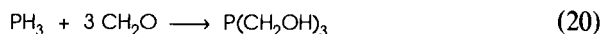


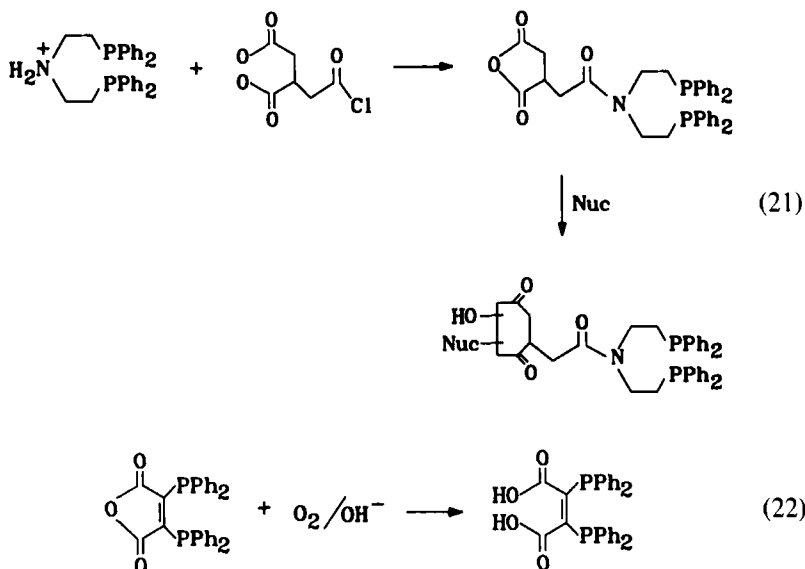
FIG. 2.



(42,43); the reaction between phosphine and formaldehyde, **5** (Eq. 20) (44); the acylation of bis[2-(diphenylphosphino)ethyl] amine followed by



reaction with a nucleophile, **6** (Eq. 21) (45); and the oxidative hydrolysis of an anhydride, **7** (Eq. 22) (46). The alkylphosphines  $\text{P}[(\text{CH}_2)_x(\text{C}_6\text{H}_5)]_3$  ( $x = 1, 2, 3, 6$ ) undergo sulfonation at both the *ortho* and *para* positions



to give water-soluble derivatives. The pure *para*-substituted compounds  $\text{P}[(\text{CH}_2)_x(\text{C}_6\text{H}_4\text{-}p\text{-SO}_3\text{Na})]_3$  can be subsequently isolated (47).

These compounds all act as regular tertiary phosphines and coordinate to metal ions via their electron pair on phosphorus. These phosphines find particular application in phase-transfer or homogeneously catalyzed reactions (Section IV-D).

### B. Metal Complexes

Water-soluble transition-metal complexes of these tertiary phosphines have been synthesized by procedures analogous to those used for phosphine complexes in nonaqueous solution. For oxygen-sensitive complexes, the high solubility of oxygen in water makes it particularly important to purge the solvent thoroughly with an inert gas prior to use. Since the tertiary phosphorus atom coordinates to form very stable complexes, only for the early transition metals must one be concerned that complexation will occur via the sulfonate group rather than via phosphorus. In essentially all cases, transition-metal complexes of these water-soluble tertiary phosphines have been synthesized for catalytic applications where water-soluble organotransition-metal complexes are important intermediates.

## IV

## HOMOGENEOUS CATALYSIS

## A. Transition-Metal Halides in Catalysis

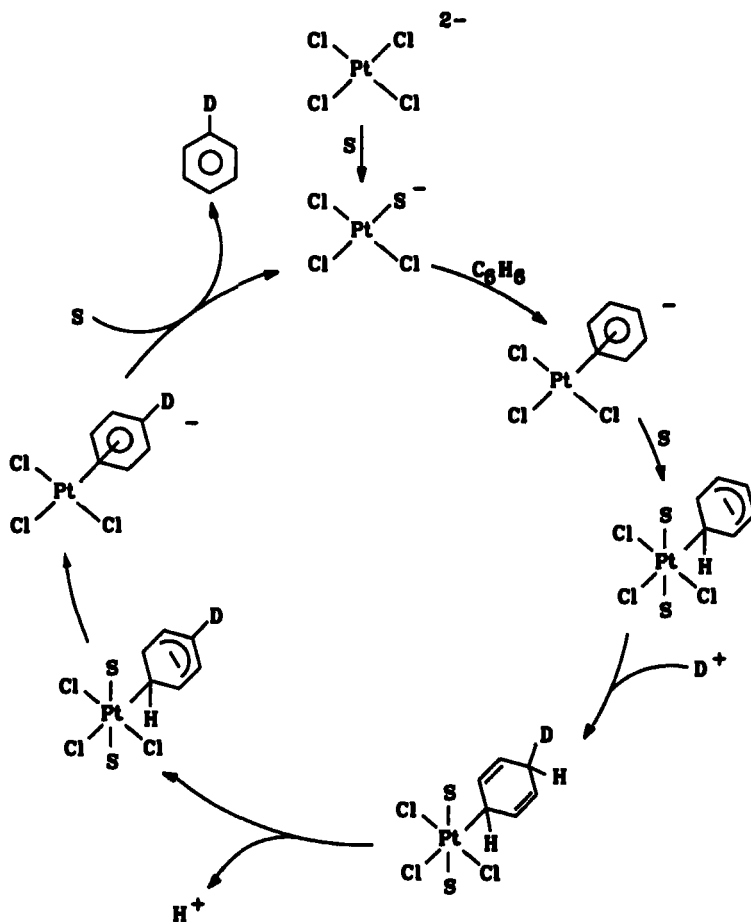
Salts of  $\text{PtCl}_4^{2-}$  in acidified aqueous solution catalyze hydrogen–deuterium exchange in arenes (48). Temperatures in the 80–100°C range are used. For the exchange reaction of benzene in  $\text{D}_2\text{O}/\text{CH}_3\text{CO}_2\text{D}$ , the rate is proportional to the concentration of both  $\text{PtCl}_4^{2-}$  and benzene, and inversely proportional to the concentration of  $\text{Cl}^-$ . The reaction is not catalyzed by the platinum(IV) complex  $\text{PtCl}_6^{2-}$  (49,50). Because substituted benzenes show an *ortho* deactivating effect, and because substituents such as nitro groups do not significantly affect the exchange rate, the dissociative mechanism shown in Scheme 8 is favored (51–53). This platinum catalyst system also catalyzes the exchange of hydrogen and deuterium in alkanes (54). The maximum rate of exchange in the alkane pentane is found for a solution containing 50 mol% acetic acid in water (55). The exchange mechanism for alkanes parallels that found for aromatics (56). The hydrogen–deuterium exchange rate increases with an increase in the carbon chain length of the *n*-alkane, with a linear correlation being observed between the logarithm of the exchange rate and the ionization potential of the alkane (55). The rate decreases with increased chain branching in the alkane, with the reactivity decreasing in the order primary > secondary > tertiary. For cyclic alkanes, the rates do not correlate with the ionization potentials; instead, steric factors are more important.

Alkanes and arenes can also be activated to other reactions by platinum complexes in aqueous solution (57,58). For arenes in the presence of  $\text{H}_2\text{PtCl}_6$ , reduction from Pt(IV) to Pt(II) occurs and the arene undergoes chlorination. The reaction is catalyzed by platinum(II) (59). Similarly, if a platinum(IV) catalyst such as  $\text{H}_2\text{PtCl}_6$  is used, chloroalkanes are formed from alkanes. As an example, chloromethane is formed from methane (Eq. 23) (60–62). Linear alkanes preferentially substitute at the methyl



group. For cyclohexanes, however, the major products are arenes, which are likely formed by dehydrochlorination of intermediate chloroalkanes. The system has been made catalytic either by the addition of  $\text{Cu}^{2+}$  and air or by the deposition of the catalyst on silica (63,64). It has been suggested that the reaction pathway involves the formation of intermediate

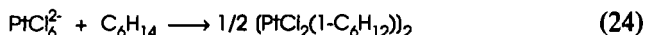




SCHEME 8.

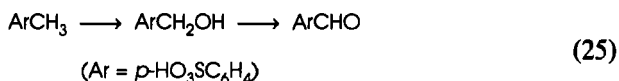
alkylplatinum(II) complexes, which subsequently react with  $\text{PtCl}_6^{2-}$  to form a carbon–chlorine bond (65).

Shilov has suggested that these catalytic reactions of alkanes involve initial addition of a C–H bond to platinum(II) to give alkyl-hydride-platinum(IV) species, which then undergo subsequent proton loss to give an alkylplatinum(II) intermediate (66). A related observation is the photolysis of a mixture of  $\text{PtCl}_6^{2-}$  and hexane in aqueous trifluoroacetic acid, leading to the formation of the 1-hexene–platinum(II) complex  $[\text{PtCl}_2(\text{C}_6\text{H}_{12})]_2$  (Eq. 24) (67). It has been proposed that this 1-hexene complex results from  $\beta$ -elimination in an alkylplatinum(IV) intermediate. The reaction is



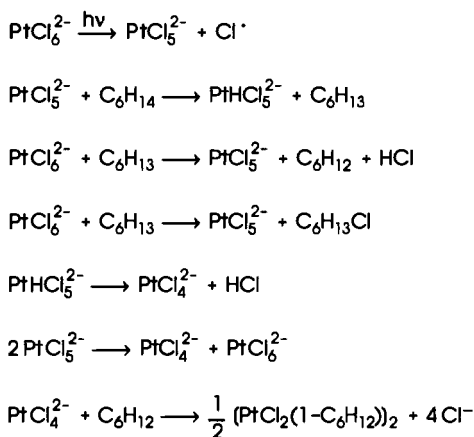
accompanied by the formation of small quantities of chlorohexane (68). An alternative explanation for these results is that the photochemical reaction follows the pathway shown in Scheme 9, which is supported by the early work of Taube showing that  $\text{PtCl}_6^{2-}$  can undergo photocatalytic redox reactions (69).

At 120°C, a mixture of  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_4^{2-}$  in the presence of oxygen can be used for the oxidation of alkanes to alcohols (70). The substrate *p*-toluenesulfonic acid is oxidized sequentially at the side-chain functionality, first to the alcohol and then to the aldehyde (Eq. 25). For ethylbenzene,



oxidation occurs both at the  $\beta$ -position, to give  $\text{ArCH}_2\text{CH}_2\text{OH}$ , and at the  $\alpha$ -position, to give  $\text{ArCH}(\text{OH})\text{CH}_3$ . This observation argues against a free-radical mechanism. When ethanol is used as substrate, ethylene glycol, acetic acid, and carbon dioxide are among the products formed.

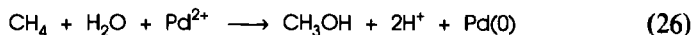
A mixture of  $\text{PtCl}_4^{2-}$  and metallic Pt with oxygen in aqueous media can be used to oxidize ethane, propane, ethers, and esters. This combination acts sequentially, whereby the initial cleavage of an unactivated C–H bond is induced by reaction with  $\text{PtCl}_4^{2-}$ . The subsequent oxidation step with oxygen is catalyzed by the metallic Pt. For ethane this sequence of



SCHEME 9.

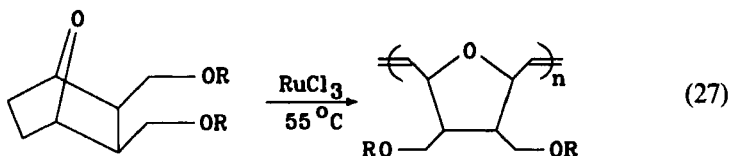
steps results in the initial formation of ethyl alcohol, which is subsequently oxidized to acetic acid (71). In the absence of metallic Pt and  $O_2$ , the oxidation of unactivated C-H bonds by  $PtCl_4^{2-}$  is still observed. For substrates with oxygen heteroatoms, the C-H bonds that are in  $\alpha$  positions to an oxygen atom are activated and catalytically oxidized by metallic Pt and  $O_2$  (72). This reaction occurs even in the absence of  $PtCl_4^{2-}$ . The selective activation and oxidation of C-H bonds in ethers by  $PtCl_4^{2-}$  follow the reactivity order  $\alpha$ -C-H <  $\beta$ -C-H <  $\gamma$ -C-H from the oxygen heteroatom. For the oxidation of ethers with  $PtCl_4^{2-}$ , the observation of an induction period makes it likely that the pathway involves the initial reduction to elemental platinum, followed by the initial C-H activation on a platinum surface rather than in aqueous solution. By judicious choice of platinum systems having either single or combinations of reagents, a series of selective hydrocarbon oxidations can be carried out, to give different products.

Palladium(II) catalysts, such as  $PdCl_4^{2-}$  in trifluoroacetic acid solvent, have been used for the conversion of methane to methanol (73). The system uses hydrogen peroxide as oxidant; the overall reaction involving the addition of one mole of water is shown in Eq. 26. The function of the



hydrogen peroxide is to reoxidize the palladium(0) back to palladium(II). The reaction sequence involves the initial formation of methyl trifluoroacetate, which is subsequently hydrolyzed to give methanol. The reaction occurs with both alkanes and arenes (74,75). These reactions show the characteristics of an electrophilic rather than a radical mechanism (76). Palladium halides such as  $PdCl_4^{2-}$  also act as catalysts for the carbonylation of aryl iodides in aqueous solution. The reaction can be used to convert aryl iodides into arene carboxylic acids under a 1-atm pressure of CO at ambient temperature (77).

Hydrated  $RuCl_3$  and  $OsCl_3$  in aqueous solution are effective catalysts for ring-opening metathesis polymerization (ROMP). An example of such a reaction is shown in Eq. 27 (78). These halides are catalyst precursors,

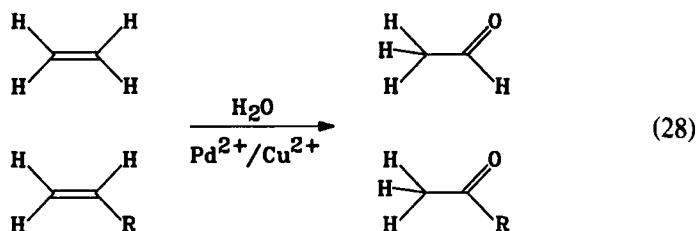


since they undergo hydrolysis to give the aquo complex  $Ru(H_2O)_6^{2+}$ , which then coordinates the double bond of the alkene to give the active complex

$\text{Ru}(\text{H}_2\text{O})_5(\text{alkene})^{2+}$ . In the absence of water these metal halides act as ROMP catalysts only after long induction periods.

### B. Wacker Oxidation of Alkenes

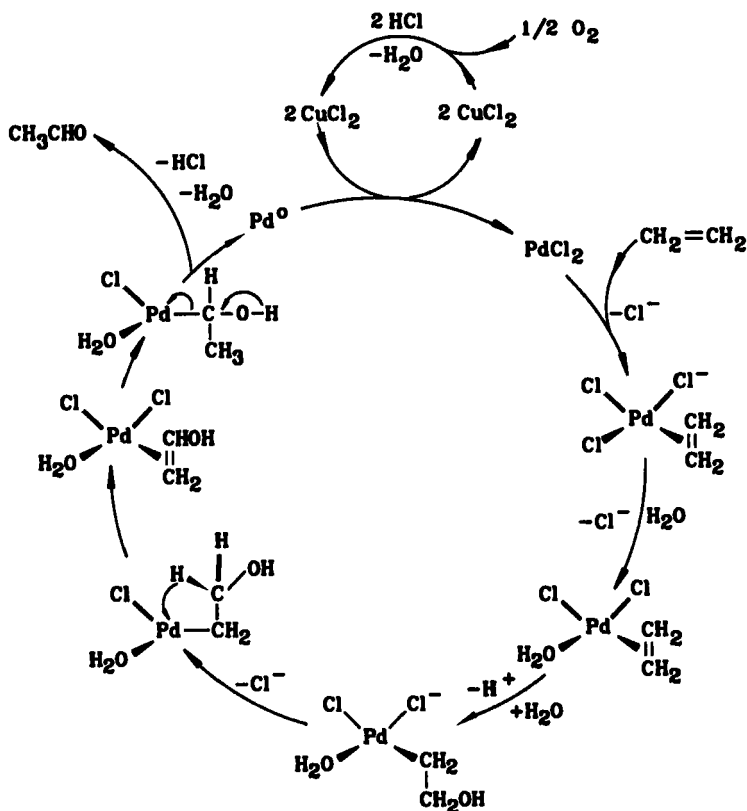
The Wacker process is an example of a homogeneously catalyzed reaction that occurs in water. The overall reaction involves the conversion of ethylene into acetaldehyde, or terminal alkenes into ketones (Eq. 28). The



reaction uses a catalyst system comprised of  $\text{PdCl}_2$ ,  $\text{CuCl}_2$ , and molecular oxygen. The mechanism involves initial coordination of the alkene to palladium(II), followed by nucleophilic attack by water at this complexed alkene. Although the details of the mechanism have not been fully elucidated, the pathway shown in Scheme 10 for the conversion of ethylene into acetaldehyde provides a reasonable description of the steps that are involved (79,80). The catalytic reaction is inhibited by  $\text{Cl}^-$ , which competes with coordination of the alkene. Following formation of the C–O bond, the organic moiety rearranges to give acetaldehyde. The pathway also involves reduction of  $\text{Pd}(\text{II})$  to  $\text{Pd}(0)$ , followed by reoxidation back to  $\text{Pd}(\text{II})$  by  $\text{Cu}(\text{II})$ . The molecular oxygen present converts the reduced  $\text{Cu}(\text{I})$  back to  $\text{Cu}(\text{II})$ . Labeling studies show that the oxygen atom in acetaldehyde or ketones originates from water rather than molecular oxygen. Since carrying out the reaction with ethylene in  $\text{D}_2\text{O}$  solvent results in no incorporation of deuterium into acetaldehyde, it is apparent that no free vinyl alcohol is formed during the reaction. Instead, the vinyl alcohol  $\beta$ -elimination product must rearrange within the coordination sphere of  $\text{Pd}(\text{II})$  before it has time to exchange with the solvent.

### C. Cobalt–Cyanide Complexes as Alkene Hydrogenation Catalysts

The cobalt(II) cyanide complex  $\text{Co}(\text{CN})_5^{3-}$  in aqueous solution acts as a homogeneous catalyst for the selective hydrogenation of conjugated dienes to monoenes (81). The initial step in this catalysis is the reaction

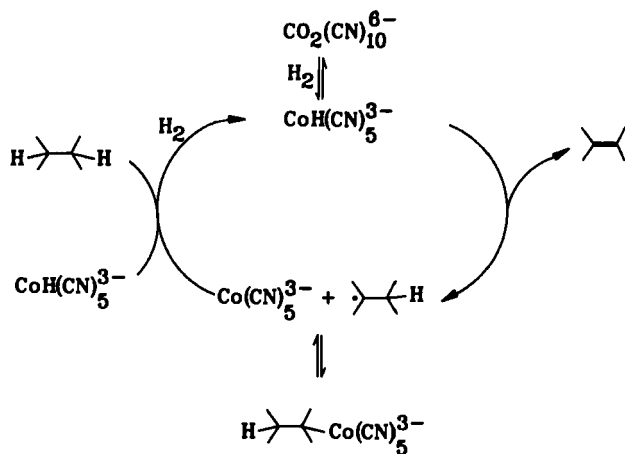


SCHEME 10.

of  $\text{Co}(\text{CN})_5^{3-}$  with hydrogen to give  $\text{CoH}(\text{CN})_5^{3-}$  (82,83). The catalytic system can be used over a temperature range of 0–125°C and a hydrogen pressure range of 1–220 atm. The reduction of carbon–carbon double and triple bonds occurs only when they are in a conjugated system. This system differs from other hydrogenation catalysts in that the pathway does not involve prior coordination of the alkene to cobalt (84). Although the detailed mechanism is complex, the major pathway is that shown in Scheme 11.

#### D. Tertiary Phosphine Complexes in Catalytic Hydroformylation and Hydrogenation Reactions

Many of the water-soluble phosphine complexes of the late transition metals that have been synthesized are designed for use as homogeneous



SCHEME 11.

hydroformylation and hydrogenation catalysts. This direction was taken in order that hydroformylation catalysts could be separated readily from the organic products of the reaction by subsequent extraction of the catalyst into an aqueous phase. A commonly used approach for incorporating water solubility into a transition-metal complex is to incorporate one or more sulfonate groups onto the organic functionalities of the phosphine. The two most frequently used water-soluble phosphines for catalytic applications are the mono- and trisulfonated triphenylphosphines, TPPMS and TPPTS, respectively (Fig. 3). Several features of ligands such as TPPTS are important when they are being considered for use in the synthesis of homogeneous catalysts. One factor is that the cone angle of TPPTS is larger than that of triphenylphosphine, which results in the formation

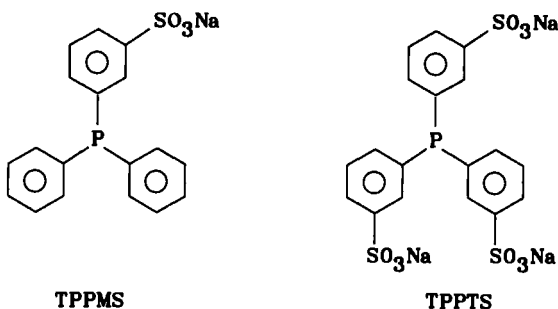


FIG. 3.

of complexes having lower coordination numbers. A second important feature, especially for solutions having a pH of 7 or above, is that hydroxy complexes may be obtained in solution. Such complexes are relatively uncommon in nonaqueous media, but in aqueous solution they are readily formed by the replacement of a coordinated  $\text{Cl}^-$  ligand by  $\text{OH}^-$  (85).

### 1. TPPMS Complexes

Transition-metal complexes of TPPMS have been used as catalysts for hydrogenation, hydroformylation, and carbonylation reactions. As an example of one such system, the complex  $\text{RhCl}(\text{TPPMS})_3$  catalyzes the hydrogenation of alkenes in neutral or slightly acidic solution (86). For this system it has been found that the *cis*-isomer maleic acid is hydrogenated more slowly than is the *trans*-isomer fumaric acid (87). This unexpected selectivity of  $\text{RhCl}(\text{TPPMS})_3$  may be due to differences in its chemistry with hydrogen as compared to that of  $\text{RhCl}(\text{PPh}_3)_3$ , a frequently used homogeneous hydrogenation catalyst in nonaqueous solution. Thus, whereas  $\text{RhCl}(\text{PPh}_3)_3$  reacts with hydrogen to give  $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$ , the complex  $\text{RhCl}(\text{TPPMS})_3$  reacts to give  $\text{RhH}(\text{TPPMS})_3$  (Eq. 29) (88). A



possible pathway for the formation of  $\text{RhH}(\text{TPPMS})_3$  involves the sequence of reactions in Scheme 12, where the final hydride complex is formed by reaction of hydrogen with the hydroxy complex. The predominance of  $\text{RhH}(\text{TPPMS})_3$  can cause significant changes in the hydrogenation mechanism. For a monohydride the final reduction step cannot involve an intramolecular reaction of an alkylhydride intermediate. Instead, the alkyl intermediate must react with either hydrogen, a molecule of  $\text{RhH}(\text{TPPMS})_3$ , or a proton. Support for the protonation route comes from the observation of extensive deuterium incorporation from the solvent  $\text{D}_2\text{O}$  in the final alkane (89). Nevertheless, this observation does not verify such a pathway, since H/D exchange between the hydride ligand in  $\text{RhH}(\text{TPPMS})_3$  and  $\text{D}^+$  may also be facile.

Aromatic and aliphatic aldehydes can be reduced to the corresponding alcohols by hydrogen transfer from formate using TPPMS complexes of

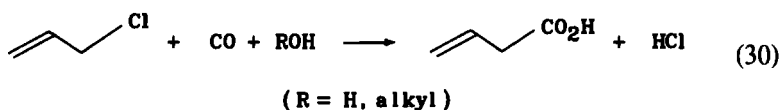


SCHEME 12.

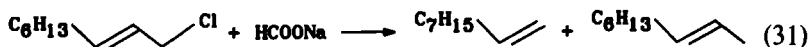
TABLE II  
CATALYTIC REDUCTION OF BENZALDEHYDE BY FORMATE AT 80°C

Catalyst	Time (min)	Conversion (%)
$\text{RuCl}_2(\text{TPPMS})_2$	20	100
$\text{RuHCl}(\text{CO})(\text{TPPMS})_3$	60	80
$\text{RuCl}_2(\text{CO})_2(\text{TPPMS})_2$	60	0
$\text{IrCl}(\text{CO})(\text{TPPMS})_3$	130	11
$\text{RhCl}(\text{TPPMS})_3$	72	22

$\text{Ru(II)}$ ,  $\text{Ru(I)}$  and  $\text{Ir(I)}$  in an aqueous medium (90). Data for the different complexes are shown in Table II. The highest conversion is observed with the ruthenium(II) complexes, which correlates with the facility of  $\text{Ru}$  complexes to catalyze other hydrogen transfer reactions. The complex  $\text{PdCl}_2(\text{TPPMS})_2$  has been used as a two-phase aqueous-organic catalyst for the carbonylation of allylic chlorides (Eq. 30) (91). The reaction pro-



ceeds smoothly under a 1-atm pressure of  $\text{CO}$ . A similar reaction of allyl chlorides and acetates with formate (Eq. 31) is also catalyzed by



$\text{PdCl}_2(\text{TPPMS})_2$  (92). In this system the water-soluble complex transports the substrate into the aqueous phase and causes it to be reduced by sodium formate. The product is a mixture of the 1- and the 2-alkene.

## 2. TPPTS Complexes as Hydroformylation Catalysts

More extensive use has been made of TPPTS than of TPPMS as a ligand for preparing water-soluble homogeneous catalysts. The major reason for this is that the presence of three sulfonate groups on TPPTS causes it to have a greater solubility in aqueous solution than does TPPMS. The principal application of TPPTS has been as a ligand for rhodium in catalyzed hydroformylation reactions. In the hydroformylation of propene with such catalyst systems, the reaction conditions use an equimolar mixture of  $\text{CO}$  and  $\text{H}_2$  at 40-bar pressure and 125°C in an aqueous solution of pH 6.0



(40,93). Excess TPPTS ligand stabilizes the system against decomposition (94). By comparison, this catalyst system is less susceptible to poisoning than is its rhodium triphenylphosphine analog. The yield of butanals is 99%, with the relative amounts of linear isomer to branched isomer being in the ratio of 94:6 (95). This selectivity ratio can be increased to 97:3 by using the sulfonated ligand shown in Fig. 4 (96). Extremely high normal: branched selectivities are also shown for the binuclear rhodium complex  $[\text{Rh}(\mu\text{-SR})(\text{CO})\text{TPPTS}]_2$ . Thus, for 1-hexene, a linear: branched aldehyde ratio of 96:4 is observed (97–101). This highest selectivity ratio is observed when  $\text{R} = \text{tert-Bu}$ , and falls to 92:8 when  $\text{R} = \text{C}_6\text{F}_5$  for the series of alkyl groups:  $\text{R} = \text{tert-Bu}$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{Me}$ ,  $\text{Ph}$ ,  $\text{C}_6\text{F}_5$ . Initially, it was believed that a cooperativity effect between the two Rh centers was playing an important role, that is, one of the steps in the hydroformylation pathway was being facilitated by the presence of a second metal center. Since for hydroformylation catalysts in nonaqueous solvent the final elimination of aldehyde involves an intermolecular reaction between rhodium acyl and hydride intermediates, there was a realistic possibility that it is this step that is accelerated by the presence of a proximal rhodium center. A problem with interpreting these results with both 1-hexene and 1-octene, however, is that under hydroformylation conditions in the presence of water the binuclear complex  $[\text{Rh}(\mu\text{-SBU})(\text{TPPTS})]_2$  is converted into  $\text{RhH}(\text{CO})(\text{TPPTS})_3$ . Any  $[\text{Rh}(\mu\text{-SBU})(\text{CO})_2]_2$  that is not converted into  $\text{RhH}(\text{CO})(\text{TPPTS})_3$  migrates into the organic phase. The introduction of the water-soluble thiol  $\text{HS}(\text{CH}_2)_3\text{NMe}_2$  gives the ionic complex  $[\text{Rh}(\mu\text{-S}(\text{CH}_2)_3\text{NHMe}_2)(\text{CO})(\text{TPPTS})]_2^+$  that does remain in the aqueous phase. This complex has a low activity level as a homogeneous hydroformylation catalyst (102).

The complex  $\text{PtCl}_2(\text{TPPTS})_2$ , when immobilized by controlled-pore glass, has been used in conjunction with  $\text{SnCl}_2$  as a hydroformyla-

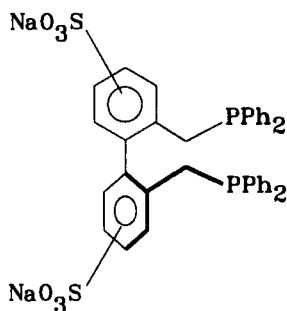


FIG. 4.

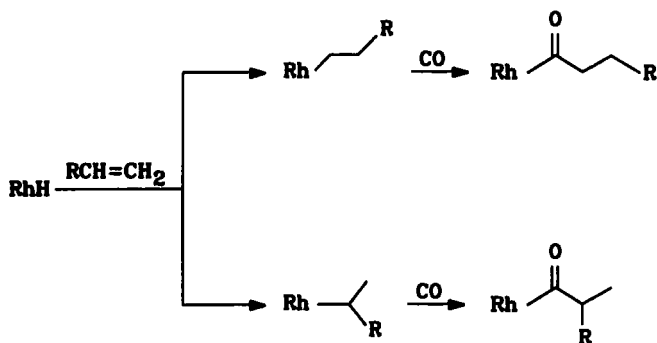
tion catalyst for 1-hexene (103). The catalytically active species is  $\text{PtCl}(\text{SnCl}_3)(\text{TPPTS})_2$ , which is adsorbed in the presence of a small amount of water. A normal : branched aldehyde ratio of 11.5 : 1 has been achieved for this hydroformylation when the catalytic reaction is carried out at a temperature of  $100^\circ\text{C}$  and a hydrogen pressure of 1000 psig.

Hydroformylations can be carried out in aqueous solution in the absence of hydrogen. Such a situation arises because these water-soluble phosphine-substituted rhodium complexes also catalyze the water-gas shift reaction (Eq. 32). Since carbon monoxide is a reagent in both the hydrofor-



mylation and the water-gas shift reaction, the initial involvement of CO in the water-gas shift reaction leads to the formation of hydrogen, which is then consumed along with CO in the subsequent hydroformylation step (100).

A comparison of homogeneous rhodium hydroformylation catalysts having either TPPTS or  $\text{PPh}_3$  as supporting ligands shows that the hydrophilic TPPTS gives higher linear : branched isomer ratios but lower overall activities than does  $\text{PPh}_3$  (104). The linear : branched isomer ratio reflects the relative amounts of linear : branched alkyl and acyl complexes that are formed in the insertion steps (Scheme 13). Higher steric requirements favor the linear isomer. Under reaction conditions using  $\text{RhH}(\text{CO})\text{L}_3$  ( $\text{L} = \text{PPh}_3$ , TPPTS) and a 200-atm pressure of CO and  $\text{H}_2$  in a 1 : 1 ratio, one difference between the two complexes is that with triphenylphosphine the substitution product  $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$  is formed, whereas with TPPTS the analog complex  $\text{RhH}(\text{CO})_2(\text{TPPTS})_2$  is not observed. This difference in the chemistries is reflected in the relative activation energies for phosphine dissociation, which is  $19 \text{ kcal mol}^{-1}$  for  $\text{PPh}_3$  and  $30 \text{ kcal mol}^{-1}$  for TPPTS.

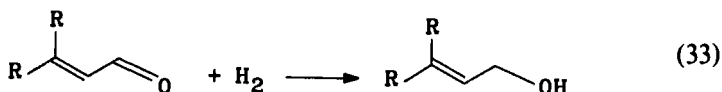


SCHEME 13.

Since these complexes are precursors to the coordinately unsaturated intermediate  $\text{RhH}(\text{CO})_2\text{L}$  ( $\text{L} = \text{PPh}_3$ , TPPTS), the presence in solution of complexes having a higher phosphine:carbon monoxide ratio for TPPTS than for  $\text{PPh}_3$ , along with the greater cone angle for TPPTS, may be the cause of the higher linear:branched ratios being found for the TPPTS rhodium hydroformylation system. In general, the  $\text{SO}_3^-$  substituents on TPPMS and TPPTS have only minimal electronic influence on the metal-phosphorus bond (105–107). The steric differences between TPPTS and  $\text{PPh}_3$ , however, are significant and can cause differences in the chemistry (33,34).

### 3. TPPTS Complexes as Hydrogenation Catalysts

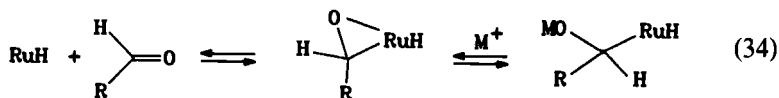
Water-soluble phosphine complexes of the late transition metals can also be used as catalysts for the hydrogenation of  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  double bonds. Thus the complex  $\text{RhCl}(\text{TPPTS})_3$  is an effective catalyst in aqueous solution for the hydrogenation of alkenes. A problem with using this complex, however, is that the TPPTS ligand is oxidized more readily than is  $\text{PPh}_3$  in  $\text{RhCl}(\text{PPh}_3)_3$ . This situation occurs because  $\text{Rh}(\text{III})$  complexes catalyze the oxygen transfer reaction from water to TPPTS to give the oxide OTPTS (108). This observation has been confirmed by the use of  $^{18}\text{OH}_2$ . Nevertheless, both the  $\text{Rh}(\text{I})$  and the  $\text{Ru}(\text{II})$  complexes of TPPTS have been used as catalysts for the homogeneous hydrogenation of the unsaturated aldehydes  $\text{RCH}=\text{CHCHO}$  (109). These homogeneous catalysts can be used for the selective reduction of  $\alpha,\beta$ -unsaturated aldehydes to unsaturated alcohols (Eq. 33).



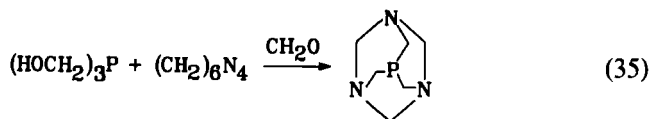
The catalytic hydrogenation of propionaldehyde in water also occurs with the series of complexes  $[\text{RuCl}_2\text{L}_2]_2$ ,  $\text{RuHClL}_3$ ,  $\text{RuH}(\text{OAc})\text{L}_3$ ,  $\text{RuH}_2\text{L}_4$ ,  $\text{RuHIL}_3$ ,  $\text{RuCl}_2(\text{CO})_2\text{L}_2$ , and  $[\text{Ru}(\text{OAc})(\text{CO})_2\text{L}]_2$  ( $\text{L} = \text{TPPTS}$ ) (110). The noncarbonylated complexes in this group all show comparable hydrogenation rates at  $100^\circ\text{C}$ . In all cases, a series of equilibria lead to the formation of  $\text{RuH}_2\text{L}_3(\text{H}_2\text{O})$ , which suggests that  $\text{RuH}_2\text{L}_3$  may be the catalytically active species.

The carbonylated complexes are less active as catalysts. The addition of alkali or alkaline earth metal ions or  $\text{NH}_4^+$  dramatically increases the activity without any loss of selectivity. For cations the rate increases in the order  $\text{NR}_4^+ < \text{Na}^+ < \text{Li}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ , and for anions the

rate increases in the order  $\text{SiF}_6^{2-} < \text{NO}_3^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ . The cation effect is believed to be due to stabilization of the C-bonded alkoxide intermediate by the binding of the cation to the  $\beta$ -oxygen (Eq. 34).



Other water-soluble tertiary phosphines can be used as ligands for the synthesis of hydrogenation catalysts. An example of such a phosphine is 1,3,5-triaza-7-phosphaadamantane, which has been prepared by reacting tris(hydroxymethyl) phosphine, formaldehyde, and hexamethylenetetramine (Eq. 35) (111,112). The ruthenium(II) complex of 1,3,5-triaza-7 phos-



phaadamantane is an effective catalyst for the catalytic hydrogenation of alkenes and aldehydes (113), and for the conversion of unsaturated aldehydes into alcohols using sodium formate as the source of hydrogen (114).

Rhodium complexes of the (2-diphenylphosphinoethyl)trimethylammonium cation have been used as both hydroformylation and hydrogenation catalysts (41). An advantage of these complexes is that they are soluble in water, and also that the ligand periphery has a cationic alkylammonium group. These two properties allow the complexes to be absorbed onto an ion exchange resin. Virtually no leaching of rhodium into the alkene-containing phases occurs with these catalysts, although the rhodium can ultimately be recovered from the resin by elution with acid (115,116).

### E. Asymmetric Catalysis with Tertiary Phosphine Complexes

Chiral-sulfonated phosphines have also been synthesized and used in the preparation of water-soluble late transition-metal complexes. These complexes, like their analogs in nonaqueous solution, can be used as homogeneous catalysts for the hydrogenation of prochiral alkenes. When the phosphine ligand has a chiral center, the alkane product can potentially be obtained in enantiomeric excess. A variety of different approaches have been used to prepare chiral phosphines that are soluble in aqueous

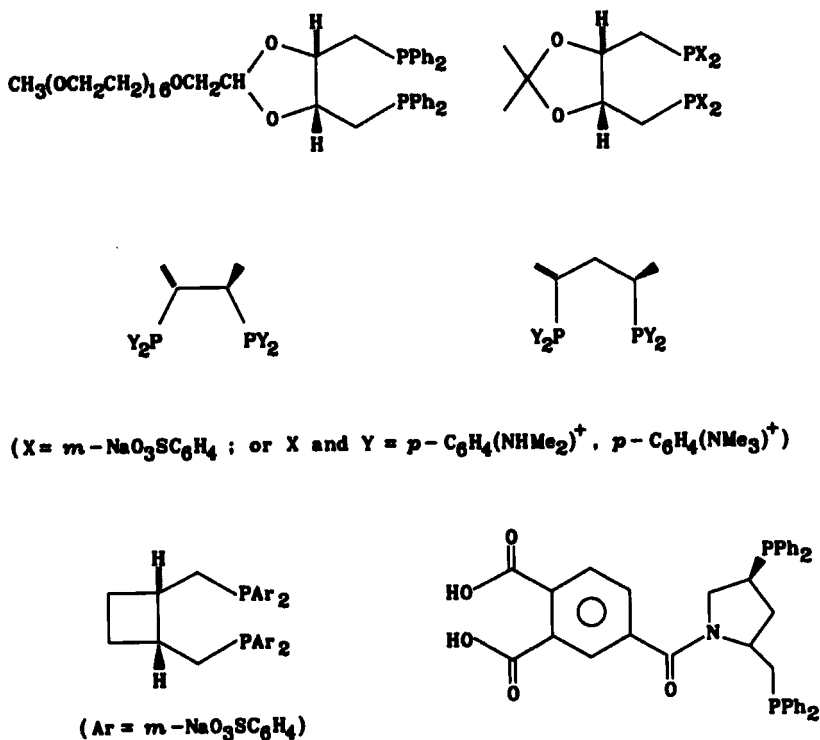


FIG. 5.

solution. As with other homogeneous hydrogenations in aqueous solution, the enantioselective hydrogenation of prochiral alkenes frequently is slow. Also, the optical yields as measured by the enantiomeric excess (ee) in the chiral alkane often are low. A series of phosphines that have been used in the synthesis of enantioselective rhodium hydrogenation catalysts are shown in Fig. 5 (45,117-121). In the absence of hydrogen as a reagent, the enantioselective reduction of alkenecarboxylic acids can be carried out with formate acting as the hydrogen transfer substrate (122).

The low enantioselectivity of chiral hydrogenation catalysts in aqueous solution has been considered to be a consequence of the effect of solvent on the key step that determines the chirality in the product alkane. For homogeneous rhodium catalysts this step is the addition of hydrogen to rhodium(I) to give a rhodium(III) species (123). A large difference between the transition-state energies for this hydrogen addition to the pair of diastereomeric  $\text{Rh(I)}$  complexes leads to the observation of a large ee in the product (Fig. 6). The low ee values found in aqueous solution can therefore

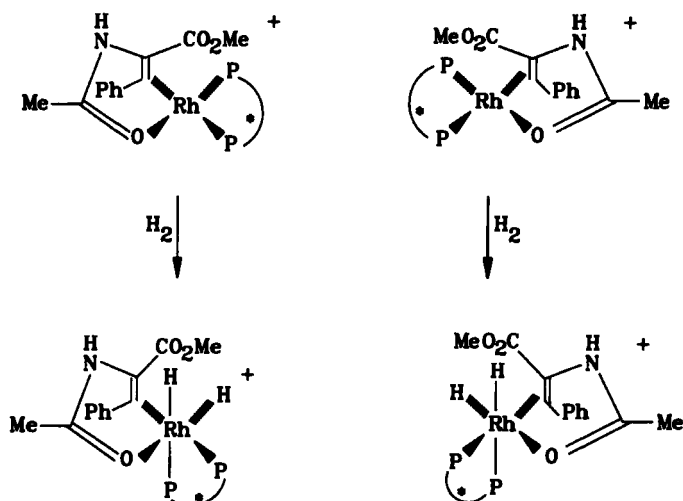


FIG. 6.

result from a small difference in these transition-state energies (124). This premise is supported by considerations that relate the observed ee with the hydrophobic and hydrophilic nature of the solvent (125,126).

Such generalizations may, however, be premature, since a comparison has also been made of the ee obtained from the hydrogenation of 2-acetamidoacrylic acid with the rhodium complexes of R-Binap(SO<sub>3</sub>Na)<sub>4</sub> and its unsulfonated analog. The ee's obtained in ethanol for the R-Binap(SO<sub>3</sub>Na)<sub>4</sub> complex (~69%) are closely comparable with those obtained for the rhodium complex of the unsulfonated R-Binap (67.0%) (127). Further evidence against such a generalization in the values of the ee's obtained in aqueous solution is also found in the observation that rhodium(I) catalysts obtained with sulfonated diphosphines yield ee's of up to 88% in the hydrogenation of carbon-carbon double bonds in a two-phase system with both an aqueous and an organic solvent system (128).

#### F. Supramolecular-Medium Effects in Catalytic Reactions

Catalytic reactions in aqueous solution can be modified by changes in the supramolecular state of the medium in which they are conducted. One approach to using medium changes to influence catalytic reactions is to introduce host molecules, such as cyclodextrins, into the reaction mixtures. Cyclodextrins have inner lipophilic cavities enclosed by hydrophilic surfaces. A cyclodextrin can bind a hydrophilic terminal alkene into its

cavity, where the alkyl chain is encapsulated and the alkene functionality is free. Such a cavity will preferentially encapsulate "rodlike" molecules; therefore, a cyclodextrin host incorporated into a hydroformylation catalyst will favor linear aldehyde formation (129).

Metal complexes of TPPMS and TPPTS have amphiphilic character because of the presence of both hydrophilic sulfonate groups and hydrophobic phenyl groups in the ligand structure. This feature allows the complex to transfer readily between the aqueous and organic phases in a biphasic system. Furthermore, these complexes can aggregate to form micelles, or surface-active compounds. This property may be a particularly important one when the properties and selectivities of catalysts formed by such phosphines are being considered (130).

Supported aqueous-phase catalysts can also be used to advantage. These supported catalysts have a thin aqueous film adhering to silica gel that contains the water-soluble complex (131). These catalysts are particularly useful for the hydroformylation of substrates such as oleyl alcohol (132). Since these catalytic reactions occur at the phase boundary, characteristics such as the water content can cause changes both in the reactivity and in the linear : branched chain ratio of the product aldehyde.

### G. Other Catalyzed Reactions

Water-soluble palladium(0) complexes have also been used as homogeneous catalysts in aqueous-solution alkylation reactions. The particular complex that has been used is  $\text{Pd}(\text{TPPMS})_3$ . Aryl or heteroaromatic halides can be coupled with aryl or vinyl boronic acids, alkynes, alkenes, or dialkyl phosphites with this palladium(0) complex. This complex in aqueous solution can also be used for the coupling of alkynes with unprotected idonucleotides, idonucleosides, and iodoamino acids (133).

Palladium(II) complexes in aqueous THF have been used as catalysts for the addition of water to the alkene diethyl maleate to give the alcohol diethyl malate. The two catalytic systems that have been used for this reaction are the dimer  $[\text{Pd}(\mu\text{-OH})\text{dppe}]_2$  and a catalyst mixture composed of  $\text{PdCl}_4^{2-}$  and  $\text{CuCl}_2$  (134). The proposed pathway for the  $[\text{Pd}(\mu\text{-OH})\text{dppe}]_2$  catalyzed reaction is that shown in Fig. 7. Any free dppe in the reaction mixture catalyzes the isomerization of diethyl maleate to diethyl fumarate. A second product of this catalytic reaction that is formed in large amounts with a  $\text{PdCl}_4^{2-}$  and  $\text{CuCl}_2$  catalyst system is the ketoester diethyl oxaloacetate. The distribution between diethyl maleate and diethyl oxaloacetate depends on the competition for an intermediate alkylpalladium(II) complex between reaction with water to give alcohol and an intramolecular  $\beta$ -elimination reaction to give the ketone (Fig. 8).

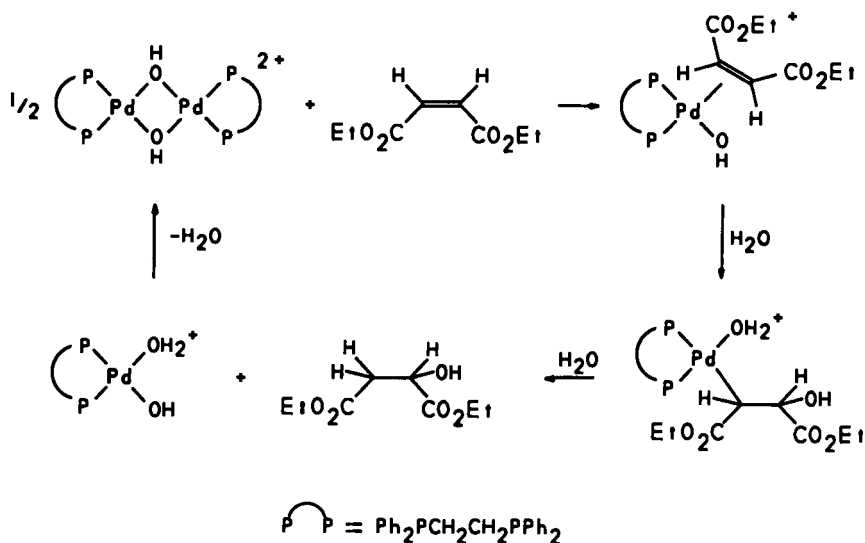


FIG. 7.

The water-soluble complex  $\text{cis-PtCl}_2(\text{TPPTS})_2$  has been used as a catalyst for the 1,4-addition of diethylamine to isoprene (Eq. 36). Water-

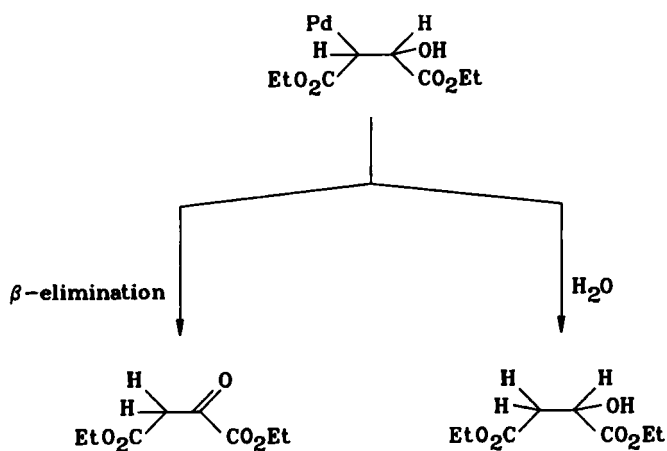
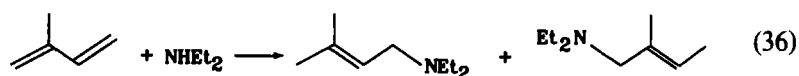


FIG. 8.



soluble rhodium complexes of TPPTS in a biphasic mixture of water and triethylamine are active catalysts for the hydrogenation of carbon dioxide to formic acid (Eq. 37) (135). The amine functions in this system to stabilize



the formic acid that is formed. Metal complexes of 2,2-bipyridine-5 sulfonic acid have been prepared as possible catalysts for the water-gas shift reaction (136).

The water-soluble zerovalent complexes  $\text{M}\{\text{P}(\text{CH}_2\text{OH})_3\}_4$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ) have been used as homogeneous catalysts for the addition of  $\text{PH}_3$  to  $\text{CH}_2\text{O}$  to give  $\text{P}(\text{CH}_2\text{OH})_3$ . No mechanistic study of the reaction has been carried out. But since aqueous solutions of  $\text{Pt}\{\text{P}(\text{CH}_2\text{OH})_3\}_4$  are in equilibrium with the hydride complex  $[\text{PtH}\{\text{P}(\text{CH}_2\text{OH})_3\}_4]\text{OH}$ , it is possible that  $\text{Pt}\{\text{P}(\text{CH}_2\text{OH})_3\}_4$  is sufficiently basic to be protonated by  $\text{PH}_3$  in one of the early steps in the catalytic cycle (137,138).

Supercritical water has the potential to be an interesting solvent system for organotransition metal systems. An example of this potential is found with the complex  $(\pi\text{-}^5\text{cp})\text{Co}(\text{CO})_2$ , which in organic solvents catalyzes the cyclotrimerization of hexyne-1, phenylacetylene, and butyne-2. At  $140^\circ\text{C}$  in aqueous media these reactions show poor selectivity to benzenes, but at  $374^\circ\text{C}$  in supercritical water the selectivity is again high (139).

#### REFERENCES

- (1) Brown, D. G. *Prog. Inorg. Chem.* **1973**, 18, 177.
- (2) Craig, P. J. (Ed.). "Organometallic Compounds in the Environment"; Wiley: New York, 1986.
- (3) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, 24, 43.
- (4) Hermann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1524.
- (5) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p. 139.
- (6) Espenson, J. H. *Acc. Chem. Res.* **1992**, 25, 222.
- (7) van Eldik, R.; Gaede, W.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1992**, 31, 3695.
- (8) Bakac, A.; Butkovic, V.; Espenson, J. H.; Orhanovic, M. *Inorg. Chem.* **1993**, 32, 5886.
- (9) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, 92, 137.
- (10) Bushey, W. R.; Espenson, J. H. *Inorg. Chem.* **1977**, 16, 2772.
- (11) Nohr, R. S.; Espenson, J. E. *J. Am. Chem. Soc.* **1975**, 97, 3392.
- (12) Meyerstein, D. *Pure Appl. Chem.* **1982**, 61, 885.
- (13) Halpern, J. *Acc. Chem. Res.* **1983**, 15, 238.
- (14) Kirker, G. W.; Bakac, A.; Espenson, J. M. *J. Am. Chem. Soc.* **1982**, 104, 1249.
- (15) Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1993**, 32, 5472.
- (16) Rotman, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1985**, 24, 4158.
- (17) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1984**, 23, 84.

- (18) Cohen, H.; Gaede, W.; Gerhard, A.; Meyerstein, D.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 3805.
- (19) Gaede, W.; Gerhard, A.; van Eldik, R.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1993**, 2065.
- (20) Cohen, A.; Feldman, A.; Ish-Shalom, R.; Meyerstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 5292.
- (21) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4157.
- (22) Sorek, Y.; Cohen, H.; Meyerstein, D. *J. Chem. Soc. Faraday Trans. 1* **1989**, *85*, 1169.
- (23) Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.
- (24) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 704.
- (25) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.
- (26) Blaser, H.-U.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 1684.
- (27) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881.
- (28) Meyerstein, D.; Schwarz, H. A. *J. Chem. Soc. Faraday Trans. 1* **1988**, *84*, 2933.
- (29) van Eldik, R.; Cohen, H.; Meyerstein, D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1158.
- (30) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55.
- (31) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607.
- (32) Avey, A.; Tyler, D. R. *Organometallics* **1992**, *11*, 3856.
- (33) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. M. *Inorg. Chem.* **1991**, *30*, 1144.
- (34) Darensbourg, D. J.; Bischoff, C. J. *Inorg. Chem.* **1993**, *32*, 47.
- (35) Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, *26*, 263.
- (36) Landon, S.; Brill, T. B. *Chem. Rev.* **1984**, *84*, 577.
- (37) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43.
- (38) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.
- (39) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219.
- (40) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570.
- (41) Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* **1982**, *62*, 135.
- (42) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3500.
- (43) Murray, R. E.; Wenzel, T. T. *Prepr. Div. Petrol. Chem., Am. Chem. Soc. Meet. Miami*, **1989**, *34*, 599.
- (44) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. J. *J. Chem. Soc. Dalton Trans.* **1993**, 269.
- (45) Nuzzo, R. G.; Haynie, S. L.; Wilson, M. E.; Whitesides, G. M. *J. Org. Chem.* **1981**, *46*, 2861.
- (46) Avey, A.; Schut, D. M.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1993**, *32*, 233.
- (47) Bartik, T.; Bartik, B.; Hanson, B. E.; Guo, I.; Toth, I. *Organometallics* **1993**, *12*, 164.
- (48) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147.
- (49) Garnett, J. L.; Hodges, R. J. *J. Am. Chem. Soc.* **1967**, *87*, 4546.
- (50) Hodges, R. J.; Garnett, J. L. *J. Phys. Chem.* **1968**, *72*, 1673.
- (51) Hodges, R. J.; Garnett, J. L. *J. Catal.* **1969**, *13*, 83.
- (52) Garnett, J. L. *Catal. Rev.* **1972**, *5*, 229.
- (53) Blackett, L.; Gold, V.; Reuben, D. M. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1869.
- (54) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174.
- (55) Hodges, R. J.; Webster, D. E.; Wells, P. B. *J. Chem. Soc. A.* **1971**, 3230.
- (56) Gol'dshleger, N. F.; Moiseev, I. I.; Khidekel, M. L.; Shteinman, A. A. *Dokl. Akad. Nauk SSSR* **1972**, *206*, 106.
- (57) Shilov, A. E. "Activation of Saturated Hydrocarbons by Transition Metal Complexes"; Reidel: Dordrecht, The Netherlands, 1984.

- (58) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
- (59) Hodges, R. J.; Garnett, J. L. *J. Phys. Chem.* **1968**, *72*, 1673.
- (60) Gol'dsleger, N. G.; Eskova, V. A.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353.
- (61) Saunders, J. R.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1975**, 1191.
- (62) Eskova, V. V.; Shilov, A. E.; Shteinman, A. A. *Kinet. Katal.* **1972**, *13*, 534.
- (63) Gol'dsleger, N. F.; Lavrushko, V. V.; Krushch, A. P.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2174.
- (64) Trateyakov, V. P.; Zimtseva, C. P.; Rudakov, E. S.; Osetskii, A. N. *React. Catal. Lett.* **1979**, *12*, 543.
- (65) Trateyakov, V. P.; Rudakov, E. S.; Bogdanov, A. V.; Zimtseva, G. P.; Kozhevina, L. I., *Dokl. Akad. Nauk SSSR* **1979**, *249*, 878.
- (66) Khrushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729.
- (67) Shulpin, G. B.; Nizova, G. V.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.* **1983**, 761.
- (68) D. M. Roundhill, Unpublished observations.
- (69) Rich, R. L.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 2608.
- (70) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628.
- (71) Sen, A.; Lin, M. *J. Chem. Soc., Chem. Commun.* **1992**, 508.
- (72) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.
- (73) Sen, A. *Platinum Met. Rev.* **1991**, *35*, 126.
- (74) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109.
- (75) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755.
- (76) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700.
- (77) Bumagin, N. A.; Nikitin, K. V.; Beletskaya, I. P. *J. Organomet. Chem.* **1988**, *358*, 563.
- (78) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.
- (79) Crabtree, R. H. "The Organometallic Chemistry of the Transition Metals"; Wiley: New York, 1987; pp. 173-176.
- (80) Elschenbroich, C.; Salzer, A. "Organometallics"; VCH: New York, 1989; pp. 425-427.
- (81) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.
- (82) De Vries, B. *J. Catal.* **1962**, *1*, 489.
- (83) Halpern, J.; Pribanic, M. *Inorg. Chem.* **1970**, *9*, 2616.
- (84) Halpern, J.; Wong, L. Y. *J. Am. Chem. Soc.* **1968**, *90*, 6665.
- (85) Herrmann, W. A.; Kulpe, J. A.; Kellner, J.; Riepl, H.; Bahrmann, H.; Konkol, W. *Angew Chem., Int. Ed. Engl.* **1990**, *29*, 391.
- (86) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1978**, *2*, 137.
- (87) Joo, F.; Somsak, L.; Beck, M. T. *J. Mol. Catal.* **1984**, *24*, 71.
- (88) Joo, F.; Csiba, P.; Benyei, A. *J. Chem. Soc., Chem Commun.* **1993**, 1602.
- (89) Laghmari, M.; Sinou, D. *J. Mol. Catal.* **1991**, *66*, L15.
- (90) Bengei, A.; Joo, F. *J. Mol. Catal.* **1980**, *58*, 151.
- (91) Kiji, J.; Okano, T.; Nishuiri, W.; Konishi, H. *Chem. Lett.* **1988**, 957.
- (92) Okano, T.; Moriyama, Y.; Konishi, H.; Kiji, J. *Chem. Lett.* **1986**, 1463.
- (93) Cornils, B.; Hibbel, J.; Konkol, W.; Lieder, B.; Much, J.; Schmidt, V.; Wiebus, E. *Eur. Pat.* 0103810, 09.7, 1983.
- (94) Rhone-Poulenc, Fr. Pat 2478 078 03.12, 1980.
- (95) Kuntz, E. J. Fr. Patent 2314910, 20.06, 1975.
- (96) Herrmann, W. A.; Kohlpainter, C. W.; Bahrmann, H.; Konkol, W. *J. Mol. Catal.* **1992**, *73*, 191.

- (97) Escaffre, P.; Thorez, A.; Kalck, P. *J. Chem. Soc., Chem. Commun.* **1987**, 146.
- (98) Escaffre, P.; Thorez, A.; Kalck, P. *New J. Chem.* **1987**, 11, 601.
- (99) Kalck, P.; Escaffre, P.; Serein Spirau, F.; Thorez, A. *New J. Chem.* **1988**, 12, 687.
- (100) Kalck, P. *Pure Appl. Chem.* **1989**, 61, 967.
- (101) Kalck, P. *Polyhedron* **1988**, 7, 2441.
- (102) Monteil, F.; Queau, R.; Kalck, R. *J. Organomet. Chem.* **1994**, 480, 177.
- (103) Guo, I.; Hanson, B. E.; Toth, I. *J. Mol. Catal.* **1991**, 70, 363.
- (104) Horvath, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. *J. Catal. Lett.* **1989**, 2, 85.
- (105) Horvath, I.; Kastrup, R.; Oswald, A.; Mozeleski, E. *Catal. Lett.* **1989**, 2, 85.
- (106) Herrmann, W. A.; Kellner, J.; Riepl, M. *J. Organomet. Chem.* **1990**, 389, 103.
- (107) Larpent, C.; Patin, M. *Appl. Organomet. Chem.* **1987**, 1, 529.
- (108) Larpent, C.; Dabard, R.; Patin, H. *Inorg. Chem.* **1987**, 26, 2922.
- (109) Grosselin, J. M.; Mercier, C.; Allmang, C.; Graes, F. *Organometallics* **1991**, 10, 2126.
- (110) Fache, E.; Santini, C. Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, 72, 331, 337.
- (111) Darensbourg, M. Y.; Daigle, D. *Inorg. Chem.* **1975**, 14, 1217.
- (112) Fisher, K. J.; Alyea, E. C.; Shahnazarian, N. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, 48, 37.
- (113) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1992**, 11, 1990.
- (114) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. M.; Daigle, D. *J. Inorg. Chem.* **1994**, 33, 200.
- (115) Smith, R. T.; Ungar, R. K.; Baird, M. C. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, 7, 288.
- (116) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, 2, 1138.
- (117) Amrani, Y.; Sinou, D. *J. Mol. Catal.* **1984**, 24, 231.
- (118) Toth, I.; Hanson, B. E. *Tetrahedron: Asymmetry* **1990** 1, 895.
- (119) Toth, I.; Hanson, B. E.; Davis, M. E. *Tetrahedron: Asymmetry* **1990**, 1, 913.
- (120) Laghmari, M.; Sinou, D. *J. Mol. Catal.* **1991** 66, L15.
- (121) Alario, F.; Amrani, Y. *J. Chem. Soc. Chem. Commun.* **1986**, 202.
- (122) Sinou, D.; Safi, M.; Claver, C.; Masdeu, A. *J. Mol. Catal.* **1991**, 68, L9.
- (123) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1986**, 102, 5952.
- (124) Amrani, Y.; Sinou, D. *J. Mol. Catal.* **1986**, 36, 319.
- (125) Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *J. Organomet. Chem.* **1989**, 370, 277.
- (126) Abraham, M. H.; Grellier, P. L.; McGill, R. A. *J. Chem. Soc., Perkin Trans. 2* **1988**, 339.
- (127) Wan, K.; Davis, M. E. *J. Chem. Soc. Chem. Commun.* **1993**, 1262.
- (128) Amari, Y.; Lecomte, L.; Sinou, D.; Bakos J.; Toth, I.; Heil, B. *Organometallics* **1989**, 8, 542.
- (129) Anderson, J. R.; Campi, E. M.; Jackson, W. R. *Catal. Lett* **1991**, 9, 55.
- (130) Hanson, B. E.; Ding, H. *46th Am. Chem. Soc. Reg. Meet.* Birmingham, AL, 1994, INOR 212.
- (131) Arhancet, J. P.; Davis, M. E.; Merola, J. S.; Hanson, B. E. *Nature (London)* **1989**, 339, 454.
- (132) Arhancet, J. P.; Davis, M. E.; Merola, J. S.; Hanson, B. E. *J. Catal.* **1990**, 121, 327.
- (133) Casalnuova A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, 112, 4324.
- (134) Ganguly, S.; Roundhill, D. M. *Organometallics* **1993**, 12, 4825.

- (135) Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465.
- (136) Herrmann, W. A.; Thiel, W. R.; Kuchler, J. G.; Behm, J.; Herdtweck, *Chem. Ber.* **1990**, 123, 1963.
- (137) Harrison, K. N.; Hoye P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096.
- (138) Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* **1992**, 31, 3026.
- (139) Jerome, K. S.; Parsons, E. J. *Organometallics* **1993**, 12, 2991.

# Structure/Property Relationships of Polystannanes

LAWRENCE R. SITA

*Searle Chemistry Laboratory  
Department of Chemistry  
University of Chicago  
Chicago, Illinois*

I.	Introduction . . . . .	189
II.	Distannanes . . . . .	190
	A. Synthesis . . . . .	191
	B. Structural Studies . . . . .	194
	C. Properties . . . . .	199
	D. Reactivity . . . . .	203
III.	Linear Polystannanes . . . . .	205
	A. Synthesis . . . . .	205
	B. Structural Studies . . . . .	208
	C. Properties . . . . .	210
	D. Reactivity . . . . .	214
IV.	Branched Polystannanes . . . . .	215
	A. Synthesis . . . . .	215
	B. Structural Studies, Properties, and Reactivity . . . . .	215
V.	Cyclopolystannanes . . . . .	217
	A. Synthesis . . . . .	217
	B. Structural Studies . . . . .	222
	C. Properties . . . . .	227
	D. Reactivity . . . . .	229
VI.	Polycyclic Polystannanes . . . . .	232
	A. Synthesis . . . . .	232
	B. Structural Studies . . . . .	234
	C. Properties and Reactivity . . . . .	237
VII.	Conclusion . . . . .	239
	References . . . . .	240

## I

## INTRODUCTION

Due to proposals that adjacent *d* and *p* orbitals can overlap to form delocalized band-type orbitals either in the ground state or the excited state (1-4), there has been much interest in the synthesis and properties of structures whose skeletal frameworks consist of covalently bonded metal atoms. However, early attempts at the rational synthesis of oligomers and polymers containing a mix of *d*- and *p*-block metals were frustrated by the general lack of synthetic methodology that can be used to prepare metal-metal bonds under relatively mild conditions, and by the

propensity of difunctional reagents to form cyclic rather than linear structures in potential polymerization processes (5). As a result, our knowledge concerning fully characterized examples of such catenated metal chains is still limited to a very small number of short oligomers containing only three to five metal atoms (5–8). In contrast, compounds whose molecular backbones consist entirely of  $\sigma$ -bonded Group 14 elements (Si, Ge, and Sn) have a rich history that extends over a wide range of structural diversity that now includes linear, cyclic, and polycyclic frameworks (9). Of these, high molecular weight polysilanes with the general formula  $X-(R_2Si)_n-X$  ( $R$  = alkyl or aryl) display a number of interesting phenomena, which include efficient photoconduction, large third-order nonlinear optical coefficients ( $X^3$ ), reversible thermochromic behavior associated with structural phase transitions, and a high degree of radiation sensitivity that makes them suitable as photoresists for microlithography (10). Accordingly, more recent attention has focused on the development of refined models that can be used to reconcile these experimental observations with theory, with the concept of “ $\sigma$ -delocalization,” as championed by Michl and others (11), gaining wide acceptance.

Although possessing intriguing properties, it can be argued that, in terms of localized molecular orbital pictures of electronic structure, polysilanes closely resemble their organic counterparts. On the other hand, polystannanes could be anticipated to display properties that are decidedly more “metal-like” in nature, possibly as a result of several factors that include, to name just a few, a greater reluctance to engage in formal  $sp$  hybridization, and a greater accessibility of  $d$  orbitals. A successful interpretation of the origins of these properties in terms of a unified molecular orbital theory, which takes into account the relativistic effects associated with heavy-atom systems, would then contribute greatly to our understanding of the molecular and electronic structure of compounds containing elements beyond the second row. Thus, it is the goal of this article to provide a comprehensive review of the extent to which theoretical and experimental investigations have probed the structure/property relationships of polystannanes. As provided in detail, this review will be limited to only those structures whose discrete skeletal frameworks consist entirely of  $\sigma$ -bonded tetracoordinate tin atoms (12).

## II

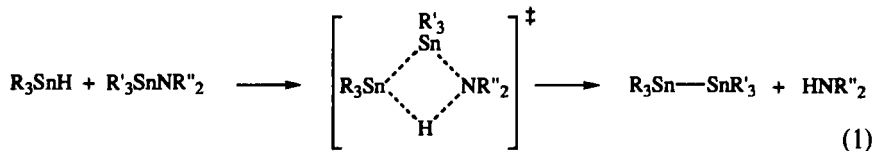
### DISTANNANES

Distannane,  $H_3Sn-SnH_3$  (1), which can be considered a heavy-atom analog of ethane, is the simplest chemical structure that falls under the preceding definition for the class of compounds known as polystannanes.

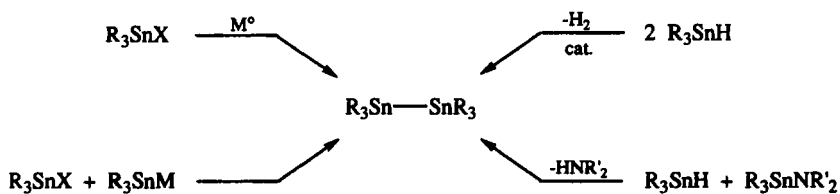
Experimentally, distannane itself is highly reactive, and attempts to obtain and study it in pure form have so far all been thwarted (13). However, it has long been known that partial or full replacement of the hydrogen atoms in **1** with organic substituents, either alkyl or aryl, imparts stability to the system; and through this mechanism then, a large number of distannane derivatives of the general formula  $R_3Sn-SnR_3$  have been prepared and their structures and properties investigated. As the discussion that follows reveals, this database of results concerning distannanes has proven to be an invaluable source of information regarding the nature of the Sn-Sn bonds in polystannane structures.

### A. Synthesis

The general synthetic methodology that can be utilized for the construction of Sn-Sn bonds in molecular compounds is summarized in Scheme 1 (14). Of these procedures, it is important to point out that the hydrostannolysis reaction, which is thought to occur through metathetical exchange between an organotin hydride and an organotin amide according to Eq. (1), is a powerful tool for the synthesis of unsymmetric distannanes of



the general formula  $R_3Sn-SnR'_3$  (15). For this class of distannane, the other methods typically provide statistical mixtures of all possible products. However, if the desired compound is a symmetric distannane, then it is often simplest to carry out either the Wurtz-type coupling of organotin halides with alkaline metals or the catalyzed dehydrogenative coupling of organotin hydrides according to Scheme 1. Both of these methods are



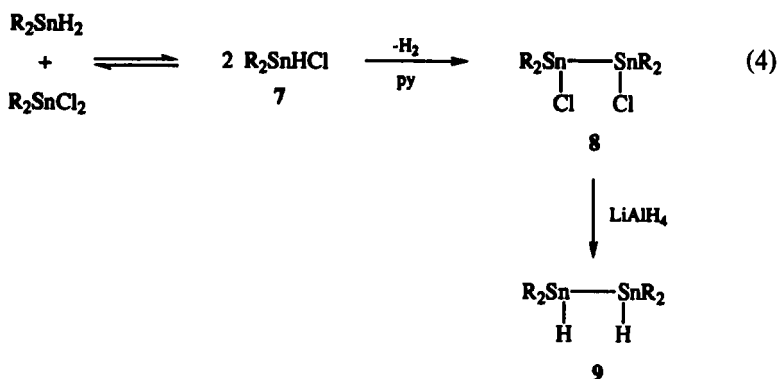
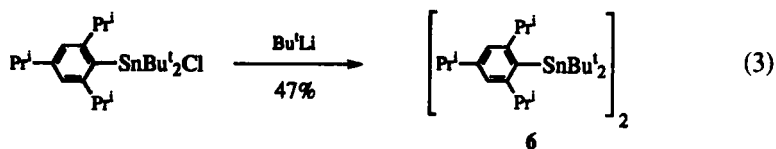
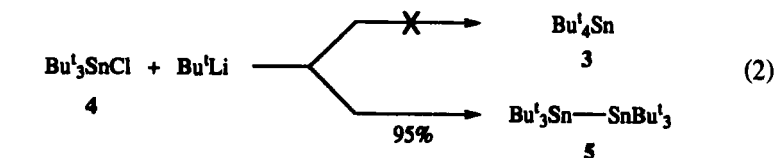
X = Cl, Br, I; M = Li, Na, K; cat. = pyridine, Pd,  $R_3N$

SCHEME 1



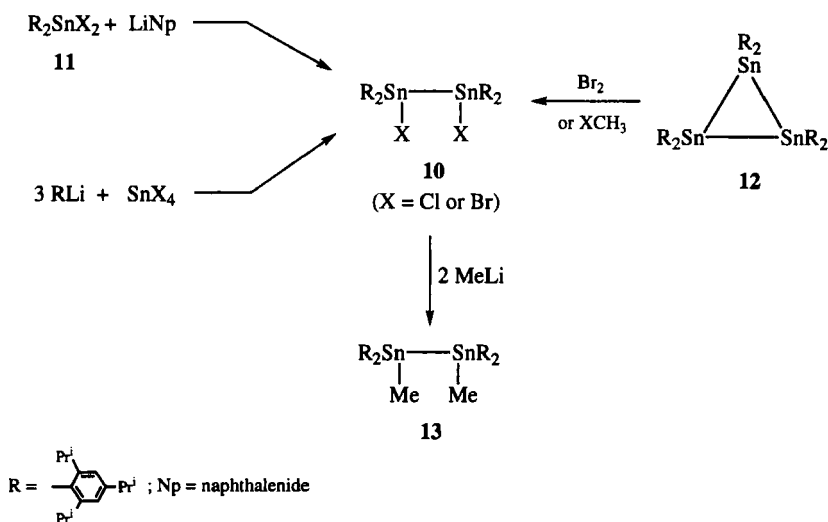
also preferable for preparing distannanes that possess substituents that are sterically demanding. Finally, it is interesting to note that the dehydrogenative coupling reaction has been successfully used to prepare the first and, to date, only example of an optically active distannane,  $[\text{Ph}(\text{PhCMe}_2\text{CH}_2)\text{MeSn}]_2$  (**2**), from the corresponding organotin hydride, which was prepared in a stereoselective manner and which is configurationally stable at the stereogenic tin center (**16**).

In addition to the general methods shown in Scheme 1 for the construction of Sn–Sn bonds, a number of distannanes have been obtained by a variety of other routes, most of which were initially discovered serendipitously (Scheme 2). For instance, in an attempt to prepare tetra(*t*-butyl)stannane (**3**) from tri(*t*-butyl)tin chloride (**4**), Kandil and Allred (**17**) found



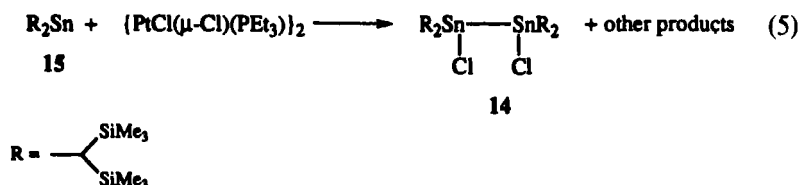
SCHEME 2

that, rather than substituting, *t*-butyllithium served to reduce **4** to provide hexa(*t*-butyl)distannane (**5**), as shown in Scheme 2 [Eq. (2)]. As determined by these authors, this side-reaction becomes the dominant pathway when the initial organotin halide is sterically encumbered, and a number of hindered distannanes have now been prepared by this method, including, more recently, 1,2-bis(2,4,6-triisopropylphenyl)-1,1,2,2-tetra(*t*-butyl)distannane **6** according to Eq. (3) (Scheme 2) (18). Taking advantage of the rapid equilibrium that is known to occur between organotin dihydrides and organotin dihalides to produce organotin hydrido halides  $R_2SnHCl$  (**7**) in solution, Neumann and co-workers (19) developed a convenient "one-pot" synthesis of 1,2-dichlorodistannanes **8** via the facile dehydrogenative coupling of **7**, which is catalyzed by pyridine [Eq. (4), Scheme 2]. These 1,2-dichloro-1,1,2,2-tetraalkyldistannanes are valuable starting materials for the synthesis of cyclic compounds containing distannane fragments (20) and for the synthesis of the 1,1,2,2-tetraalkyldistannanes **9** ( $R = Bu$  and *i*-Bu) via reaction with lithium aluminum hydride (19). Regarding hindered 1,2-dihalodistannanes, there now exists several different routes to 1,2-dichloro- and 1,2-dibromo-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane **10**. These include the reductive coupling of the corresponding diorganotin dichloride **11** with lithium naphthalenide (21) or directly from  $SnX_4$  ( $X = Cl$  or  $Br$ ) and the corresponding aryllithium reagent (22) (Scheme 3). Compound **10** has also been prepared from the

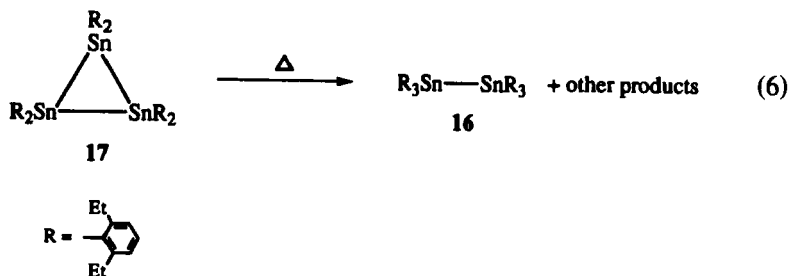


SCHEME 3

halogenation of hexakis(2,4,6-triisopropyl-phenyl)cyclotristannane **12** (21) using either bromine (23) or the respective haloforms (24). With alkyl-lithium reagents of small steric bulk, compound **10** ( $X = \text{Cl}$ ) has in turn been used to prepare 1,2-dimethyl-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane **13**, as shown in Scheme 3 (24). Finally, it must be mentioned that a few distannanes have been isolated as either by-products or products of decomposition pathways. These include the isolation of 1,2-dichloro-1,1,2,2-tetrakis[bis(trimethylsilyl)methyl]distannane **14** from the reaction of the stable stannylene derivative, bis[bis(trimethylsilyl)methyl]-tin **15** (25), with the  $\text{Pt}^{\text{II}}$  substrate,  $\{\text{PtCl}(\mu\text{-Cl})(\text{PEt}_3)\}_2$  [Eq. (5)] (26), and



the isolation of hexakis(2,6-diethylphenyl)distannane **16** from the thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane **17** (27) either in the solid state or in solution (28) [Eq. (6)].




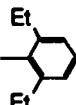
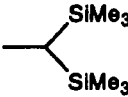
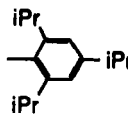
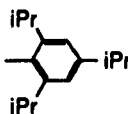
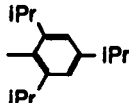


## B. Structural Studies

### 1. Peraryl Derivatives

As predicted by theoretical calculations, the force constant for Sn–Sn bond stretching in distannane is quite small (29), and thus, for synthetic derivatives that possess severe nonbonded steric interactions between substituents, elongation of the Sn–Sn bond is observed in the set of solid-state structural parameters for these compounds. Given this, as Table I indicates, there has been much current interest in probing the limit to

TABLE I  
SELECTED BOND LENGTHS AND TORSION ANGLES FOR DISTANNANES

Compound	Bond lengths (Å)		Torsion angles (°)		Ref.
	Sn-Sn	Sn-C (avg)	C-Sn-Sn-C	Sn-Sn-C <sub>Ph</sub> -C <sub>Ph</sub>	
$R_3Sn-SnR_3$ <i>Peraryl</i>					
$R =$  (18)	2.770	2.180	60	13, 23, 45	(30)
$R =$  Me (19)	2.777	2.150	87, 33	42, 58	(33a,b)
$R =$  Me (20)	2.883	2.168	60	53, 54, 56	(34)
$R =$  Et Et (16)	3.052	2.243	63, 61, 56	48, 51, 55	(28)
<i>Peralkyl</i>					
$R =$ benzyl (21)	2.823	2.191	60	—	(24)
$R =$ <i>t</i> -butyl (5)	2.894	2.238	75, 44	—	(24)
$RR'R''Sn-SnRR'R''$ $R = R' = Me; R' = Cl$ (8)	2.770	2.14	130.1, 13.5	—	(36)
$R = R' =$  (14) $R'' = Cl$	2.844	2.19	~60	—	(26)
$R = R' =$  (10) $R'' = Br$	2.841	2.191	~60	—	(22,24)
$R = R' =$  (13) $R'' = Me$	2.829	2.22, 2.18	77, 43	—	(18)
$R =$  (6) $R' = R'' = t-Bu$	3.034	2.259	5.1, 5.6, 21.1	—	(18)

which this bond length distortion can be forced and still maintain a stable distannane structure. In this regard, the Sn–Sn bond length of 2.770 Å determined for the crystal structure of hexaphenyldistannane (**18**) is often taken as the reference point, since this value is fairly close to the one calculated for the parent compound (*cf.* 2.804 Å) (29,30). Another feature of the structure of **18** is how the nonbonded interactions between the phenyl groups dictate this compound's symmetry properties in the solid state. As pointed out by Mislow and co-workers (31), **18** can potentially exist in two distinct conformations that are defined by the helical sense of the "propeller-like"  $\text{Ph}_3\text{Sn}$  moieties when viewed along the threefold axis of the molecule. One of these conformations is achiral (*meso*), with point group symmetry  $S_6$ , in which the two moieties are heterochiral, i.e., have opposite helicities, while the other conformation is chiral, with point group symmetry  $D_3$ , in which the two moieties are homochiral, i.e., have the same helicity. For **18**, only a staggered  $S_6$  conformation is observed in the solid state, either as a result of its being the lowest-energy structure or as a result of crystal packing forces that enforce it over a  $D_3$  conformation. Evidence that, due to the calculated small barrier to rotation about the Sn–Sn bond in the parent distannane **1** (32), these latter solid-state interactions can play a significant role in influencing the geometrical parameters of distannanes is provided by the crystal structure of hexa(4-methylphenyl)distannane **19** (33*a,b*). Thus, as Fig. 1*a* reveals, the molecular structure of **19** is still one in which the opposing  $\text{R}_3\text{Sn}$  moieties have helicities of opposite chirality, as in **18**; but now instead of a similar fully staggered conformation, **19** adopts one in which the torsion angles are 87.33° and 32.67°, respectively. Interestingly, it appears that by increasing the tilt angle of the phenyl groups from 20° to 55°, the expected increase in nonbonded interactions brought about by the closer proximity of the phenyl groups on the adjacent tin atoms in this conformation can be accommodated without significantly distorting bond lengths [*cf.* Sn–Sn, 2.777 Å; Sn–C, 2.150 Å for **19** (Table I)].

In compound **19**, the steric influence of the 4-methyl groups on the aromatic substituents should be, and apparently are, negligible. However, the placement of groups at *ortho* positions should have profound effects; and indeed, this assertion is supported by the structural parameters shown in Table I and Fig. 1*b* for the isomeric compound hexa(2-methylphenyl)distannane (**20**) (34). Once more, only a staggered  $S_6$  structure is observed in the solid state for compound **20**. However, now due to severe nonbonded interactions between substituents that cannot be relieved by further tilting of the phenyl groups, the Sn–Sn bond length has been substantially elongated to 2.883 Å. Furthermore, from an analysis of this structure, it is

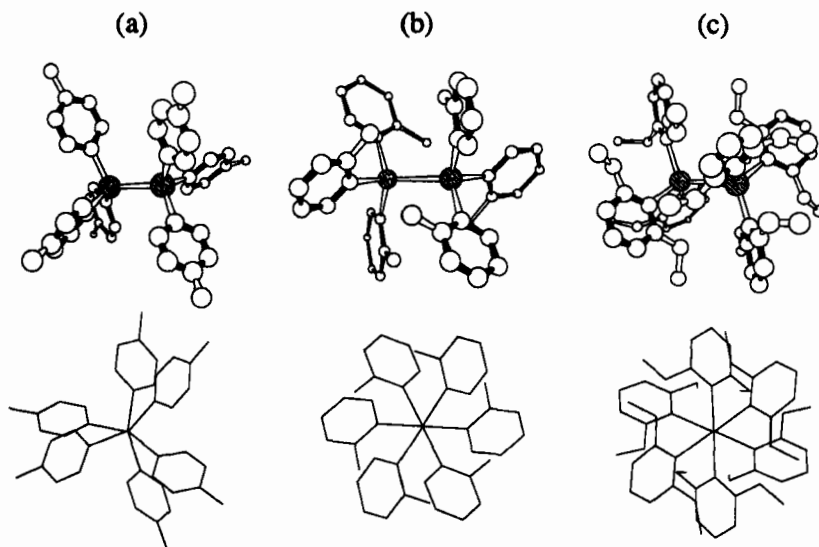


FIG. 1. Molecular structures of: (a) hexakis(4-methylphenyl)distannane (**19**), (b) hexakis(2-methylphenyl)distannane (**20**), and (c) hexakis(2,6-diethylphenyl)distannane (**16**). Structures redrawn from coordinates provided in references 33, 34, and 28, respectively.

clear that a  $D_3$  conformation for **20** would be even more strained, due to an increase in nonbonded interactions.

A good example of how far the Sn–Sn bond of distannanes can be elongated and still obtain a stable structure is provided by the crystal structure of hexakis(2,6-diethylphenyl) distannane **16** (35). As Table I and Fig. 1c reveal, both the Sn–Sn and the mean Sn–C bond lengths, at 3.052 and 2.243 Å, respectively, are now dramatically elongated relative to **18**. Not surprisingly, to relieve best the strong nonbonded interactions present in this compound, the structure is the fully staggered  $S_6$  conformation observed previously. In addition, it becomes clear that a 55–57° tilt of the phenyl groups is likely to be the maximum that can be accommodated in sterically encumbered peraryl distannane derivatives.

## 2. Peralkyl Derivatives

The body of structural data for peralkyl distannanes is a little more sparse than that for peraryl derivatives, with only two crystal structures

having been determined. However, through a comparison of these two structures, a similar trend regarding the impact of nonbonded steric interactions on Sn–Sn bond length can be observed. Thus, the solid-state structure of hexabenzylidistannane **21** reveals a Sn–Sn bond length of 2.823 Å for a fully staggered conformation (Table I) (24). In contrast, the molecular structure of hexa(*t*-butyl)distannane **5** possesses a Sn–Sn bond that has now been elongated to 2.894 Å by virtue of the strong steric interactions between the branched alkyl substituents on adjacent tin atoms (Table I) (24). In this latter structure it is interesting to note that a more eclipsed conformation is adopted with torsional angles of 77° and 45°, respectively. The molecular structures of compounds **5** and **21** are shown in Fig. 2.

### 3. Mixed Derivatives

In addition to the peraryl and peralkyl derivatives already described, the crystal structures for a number of distannanes with mixed types of substituents, including halogens, have been determined (Table I). For the most part, the geometric parameters and solid-state conformations of these compounds are in keeping with what has been presented so far. However,

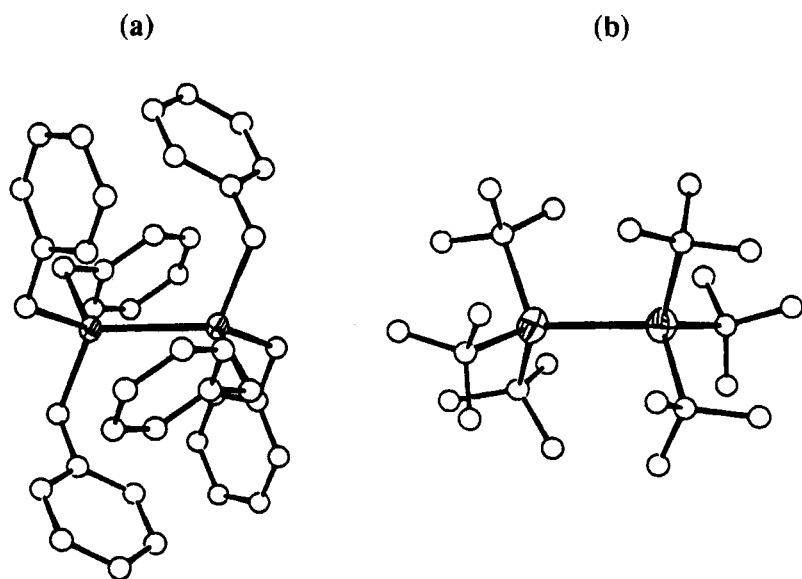


FIG. 2. Molecular structures of: (a) hexabenzylidistannane (**21**) and (b) hexa(*t*-butyl)distanthane (**5**). Reprinted with permission from Puff *et al.* (24).

some unique features of these structures deserve comment. To begin with, the molecular structure of 1,2-dichloro-1,1,2,2-tetramethyldistannane **8** ( $R = \text{Me}$ ) displays a normal Sn–Sn bond length of 2.770 Å, but due to strong Sn---Cl intermolecular interactions (Sn---Cl, 3.240 Å vs Sn–Cl, 2.448 Å), this compound is polymeric in the solid state. As a result, the methyl substituents on the adjacent tin atoms are nearly eclipsed (smallest torsion angle, 13.5°) (36). In contrast to what is observed for **8**, by increasing the steric bulk of the organic substituents, intermolecular interactions between tin and a halogen atom can be prevented, and as a result these distannanes remain monomeric in the solid state. Examples of distannanes that fall into this category are provided by 1,2-dichloro-1,1,2,2-tetrakis[bis(trimethylsilyl)methyl]distannane **14** (26) and 1,2-dibromo-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane **10** (22,24). Both of these compounds adopt nearly staggered conformations, with Sn–Sn bond lengths that are only moderately distorted (Sn–Sn, 2.844 Å for **14** and 2.841 Å for **10**).

A final class of distannanes to consider are those that possess a mixture of aryl and alkyl substituents. In this regard, the structures of two derivatives are known. One of these is represented by 1,2-dimethyl-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane **13**, which is conveniently prepared from the corresponding 1,2-dichloro derivative (24). This compound adopts a solid-state conformation that is more eclipsed (mean torsion angles, 77° and 43°, respectively) and that has a Sn–Sn bond length of 2.829 Å (Table I). The other compound that falls into this class is 1,2-bis(2,4,6-triisopropylphenyl)-1,1,2,2-tetra(*t*-butyl)distannane **6**. This compound surprisingly adopts a nearly eclipsed conformation, with a very long Sn–Sn bond length of 3.034 Å, which is nearly as long as that of the distannane **16** (Table I and Fig. 3) (18). Apparently, it is this conformation that can best relieve the strong steric interactions between the two aryl substituents.

### C. Properties

#### 1. Electronic and Vibrational Spectroscopy

It has long been known that the electronic spectrum of hexaphenyldistannane (**18**) exhibits a strong absorption maximum ( $\lambda_{\text{max}}$  247 nm;  $\epsilon_{\text{max}}$  40,400), which has been attributed to the presence of the Sn–Sn bond in this compound (37,38). If this absorption feature correlates with a  $\sigma_{\text{Sn-Sn}} \rightarrow \sigma_{\text{Sn-Sn}}^*$  transition, then one might expect to observe a Sn–Sn bond length dependence on its strength and position. Indeed, the observation that it has shifted to 287 nm ( $\epsilon_{\text{max}}$  20,382) in the sterically encumbered



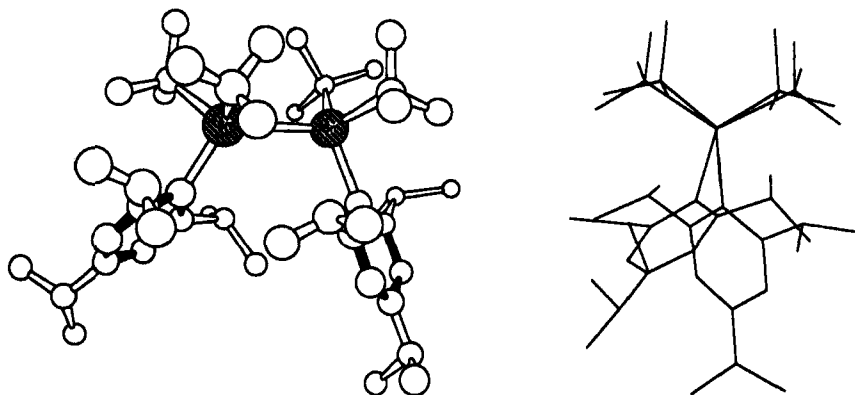



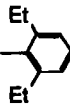


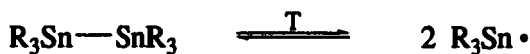
FIG. 3. Molecular structure of distannane **13**. Structure redrawn from coordinates provided in Weidenbruch *et al.* (18).

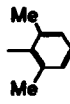
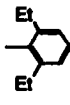
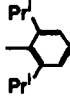
distannane **16** (Sn–Sn; 3.052Å) seems to lend support to this assignment (Table II) (39). For peralkyl distannane derivatives, this absorption maximum is blue-shifted (*cf.* for R = Me and cyclohexyl in Table II), possibly as a result of a smaller degree of polarizability of the alkyl vs aryl substituents. However, it is interesting to note that for hexabenzylidistannane (**21**) it is almost identical to that of compound **18** (Table II). Clearly, the origin and nature of substituent effects on this unique electronic transition in distannanes is a subject for more thorough theoretical and experimental investigation.

As mentioned previously, the calculated force constant for Sn–Sn bond stretching in distannane (**1**) is quite small, and the harmonic frequency associated with this bond length deformation is predicted to lie at 189  $\text{cm}^{-1}$  (29). This value is in quite excellent agreement with the value of 208  $\text{cm}^{-1}$  that was obtained from the Raman spectrum of hexamethyldistannane (**22**) (40). However, a dramatic perturbation occurs upon phenyl substitution, as revealed by the value of 138  $\text{cm}^{-1}$  that is experimentally obtained for hexaphenyldistannane **18** (Table II). Not surprisingly, there also appears to be a strong correlation between nonbonded steric interactions and bond stretching frequency in distannanes. This is most readily observable in making the comparison between compounds **18** and **20** (*cf.*  $\nu(\text{Sn–Sn})$  138  $\text{cm}^{-1}$  vs 123  $\text{cm}^{-1}$ , respectively) (Table II). Indeed, Neumann and co-workers (41 *a,b*) correlated bond-stretch frequency with Sn–Sn bond dissociation energies for the peraryl distannanes **23–25**, which they showed dissociated reversibly to the corresponding triaryltin radicals at decreasing temperatures along the series, due to an increasing amount of nonbonded interactions between the organic substituents (Scheme 4).

TABLE II  
ELECTRONIC AND VIBRATIONAL SPECTRA FOR SELECTED DISTANNANES

Compound: $R_3Sn-SnR_3$	UV		Raman ( $cm^{-1}$ ) $\nu(Sn-Sn)$	Sn-Sn ( $\text{\AA}$ )
	$\lambda_{max}$ (nm)	$\epsilon_{max}$		
$R = $  (18)	248	40,400	138	2.770
$R = $  -Me (19)	248	40,400	131	2.777
$R = $  (20)	—	—	123	2.883
$R = $  (16)	287	20,382	—	3.052
$R = $ Me (22)	<215	—	208	—
$R = $ cyclohexyl	<220	>34,500	133	—
$R = $ <i>t</i> -butyl (5)	222	59,000	115	2.894
$R = $ benzyl (21)	247	40,600	—	2.823



$R_3Sn-SnR_3$	$\Delta H$ (kcal mol $^{-1}$ )	T ( $^{\circ}C$ )	$\nu(Sn-Sn)$ (cm $^{-1}$ )
$R = $  (23)	$49 \pm 2$	180	102
$R = $  (24)	$26.6 \pm 2$	100	92
$R = $  (25)	$8.5 \pm 1$	20	—

SCHEME 4

Thus, compound **23**, with a  $\nu(\text{Sn-Sn})$  of  $102\text{ cm}^{-1}$ , appears to thermally dissociate beginning at  $180^\circ\text{C}$ , compound **24** at  $100^\circ\text{C}$  [ $\nu(\text{Sn-Sn})$   $92\text{ cm}^{-1}$ ], and finally, compound **25**, for which  $\nu(\text{Sn-Sn})$  cannot be measured, at only  $20^\circ\text{C}$ . Unfortunately, the structural parameters and the electronic spectra for compounds **23-25** have not yet been obtained, so a correlation between these parameters and their Sn-Sn bond lengths cannot be made.

## 2. $^{119}\text{Sn}$ Nuclear Magnetic Resonance (NMR) Spectroscopy

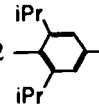
Due to the occurrence of two isotopes of tin with  $I = 1/2$ ,  $^{119}\text{Sn}$  and  $^{117}\text{Sn}$ , of relatively high natural abundance (8.58% and 7.61%, respectively) and high receptivity (natural abundance times sensitivity) (25.6 and 19.9, respectively) relative to  $^{13}\text{C}$  ( $= 1$ ),  $^{119}\text{Sn}$  NMR spectroscopy is a powerful tool for the investigation of tin-containing compounds (42 *a,b*). This is especially true for polystannanes, where  $^n\text{J}(^{119}\text{Sn}-^{117}\text{Sn})$  coupling constants between magnetically equivalent tin atoms can still be obtained and the corresponding  $^n\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  values derived [via the relationship  $^n\text{J}(^{119}\text{Sn}-^{119}\text{Sn})/^n\text{J}(^{119}\text{Sn}-^{117}\text{Sn}) = 1.046$ ].

As Table III indicates, the nature of the substituents in distannanes can influence both the chemical shift ( $\delta$ ; referenced relative to tetramethyltin) and the direct one-bond coupling constant,  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$ . The influence of substituents on chemical shifts has been discussed in detail elsewhere (42 *a*); therefore, an in-depth analysis of the nature of this influence will not be repeated here. However, the influence of substituents on the  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  values deserves some comment (43-44 *a-c*). In the case of peralkyldistannanes (Table III), it has been proposed that from an apparent linear correlation between  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  and  $\Sigma\sigma^*$  (the sum of the Taft  $\sigma^*$  constants of the six alkyl groups bound to the tin atoms), the main factor involved in determining the value of  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  in these compounds is  $Z_{\text{eff}}$ , the effective nuclear charge at the tin nucleus (43 *a,b*). However, an alternative proposal to explain the trend observed in Table III is based on the equation derived by Pople and Santry (45) for the coupling mechanism in a two-body spin system [Eq. (7)]. Here,  $\Psi_{\text{ns}}(0)$

$$^1J_{\text{XY}} = \frac{16\beta^2}{9\gamma_{\text{X}}\gamma_{\text{Yh}}} \cdot \Psi_{\text{ns(X)}}^2(0) \cdot \Psi_{\text{ns(Y)}}^2(0) \cdot \pi_{\text{XY}} \quad (7)$$

is the valence  $s$  electron density at the nucleus and  $\pi_{\text{XY}}$  is the mutual polarizability of the atoms X and Y. Since  $\pi_{\text{XY}}$  is related to the valence  $s$ -overlap integral  $\beta$  between X and Y, it has been argued that the increase in nonbonded interactions that occurs with increasing  $\alpha$ -branching of the

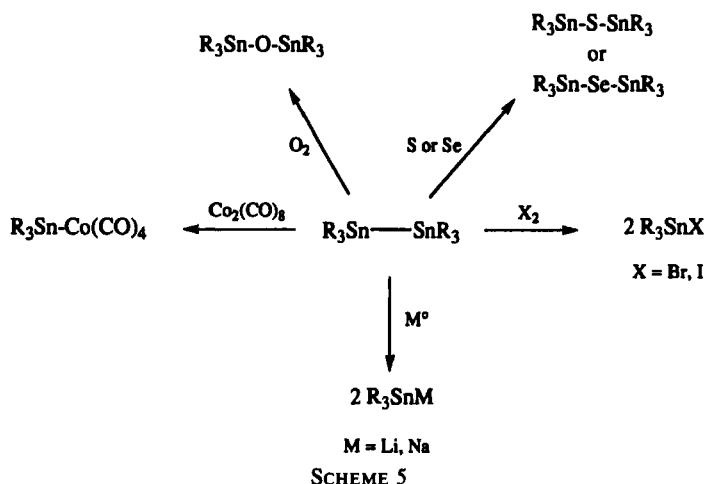
TABLE III  
 $^{119}\text{Sn}$  NMR DATA FOR DISTANNANES

Compound: $\text{R}_3\text{Sn-SnR}_3$	$\delta$ (ppm)	$^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$ (Hz)
$\text{R} = \text{—C}_6\text{H}_5$ ( <b>18</b> )	−144.7	4480
$\text{R} = \text{—C}_6\text{H}_4\text{—Me}$ ( <b>19</b> )	−141.9	4570
$\text{R} = \text{—C}_6\text{H}_4\text{—Me}$ ( <b>20</b> )	−136.8	4297
$\text{R}_3 = \text{Br}$ , 2  ( <b>10</b> )	−118.3	5212
$\text{R} = \text{Me}$ ( <b>22</b> )	−108.7	4211
$\text{R} = \text{Bu}$	−83.2	2625
$\text{R} = \text{Pr}^i$	−29.1	1155
$\text{R}_3 = \text{Pr}_2^i, \text{Bu}^i$	−21.5	730
$\text{R} = \text{Bu}^i$ ( <b>5</b> )	−6.1	57
$\text{R} = \text{Benzyl}$ ( <b>21</b> )	−44.6	1780

alkyl substituents in distannanes leads to a diminishing of  $\beta$ , and in turn, to the magnitude of  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  (44 *a-c*). Interestingly, in the case of peraryldistannanes,  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn})$  seems to be much less sensitive to an increase in Sn–Sn bond length brought about by an increase in steric interactions [*cf.*  $^1\text{J}(^{119}\text{Sn}-^{119}\text{Sn}) = 4480$  Hz for hexaphenyldistannane **18** vs a value of 4297 Hz for hexakis(2-methylphenyl)distannane **20** (Table III)].

#### D. Reactivity

The chemical reactivity of the Sn–Sn bond has also been amply reviewed, and some of the more common reactions involving this moiety are shown in Scheme 5 (13). Of these, the reductive cleavage of distannanes with alkaline metals has been used as a convenient source of the corresponding triorganotin anions,  $\text{R}_3\text{SnM}$ , and these have found utility in the preparation of a number of organotin compounds that are useful for organic synthesis, especially for the case where  $\text{R} = \text{Me}$  or  $\text{Bu}$  (46). Concerning the strength of the Sn–Sn bond in distannanes,  $\Delta H_{\text{diss}}$  has



been estimated to be about  $66 \text{ kcal mol}^{-1}$  in hexamethyldistannane (**22**) (**47**), and simple hexaalkyldistannanes can be distilled without decomposition. As previously discussed, only when severe nonbonded interactions between substituents are present, as in the compounds **23–25**, does one observe facile bond dissociation in solution. On the other hand, homolysis of the  $Sn-Sn$  bond occurs readily when distannanes are irradiated with ultraviolet light. It has also been observed that the halide-containing distannanes,  $R_3SnSnR_2Br$  ( $R = Me$  and  $Et$ ) and 1,2-dichloro-1,1,2,2-tetramethyldistannane (**8**), thermally decompose at fairly low temperatures (**48**). With oxygen, distannanes react to provide the corresponding distannoxanes,  $R_3Sn-O-SnR_3$ . Sulphur and selenium can similarly be inserted into the  $Sn-Sn$  bond, and while peralkyl distannanes are typically more reactive than peraryl ones, bulky substituents can retard these reactions by raising energy barriers for bimolecular processes. The use of sterically demanding substituents is, in fact, the basis for a strategy known as *kinetic stabilization*, which has been successfully employed for the synthesis of polystannane frameworks that would normally have highly reactive  $Sn-Sn$  bonds. Finally, a few other reactions of distannanes deserve comment. First, halogens typically react rapidly and quantitatively (**33a**), and titration with iodine or bromine can be used for estimating the  $Sn-Sn$  bond content of polystannanes. In addition, a variety of transition-metal compounds react with distannanes to form triorganotin-transition-metal complexes (**42b**).

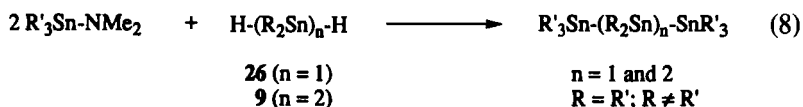
## III

## LINEAR POLYSTANNANES

## A. Synthesis

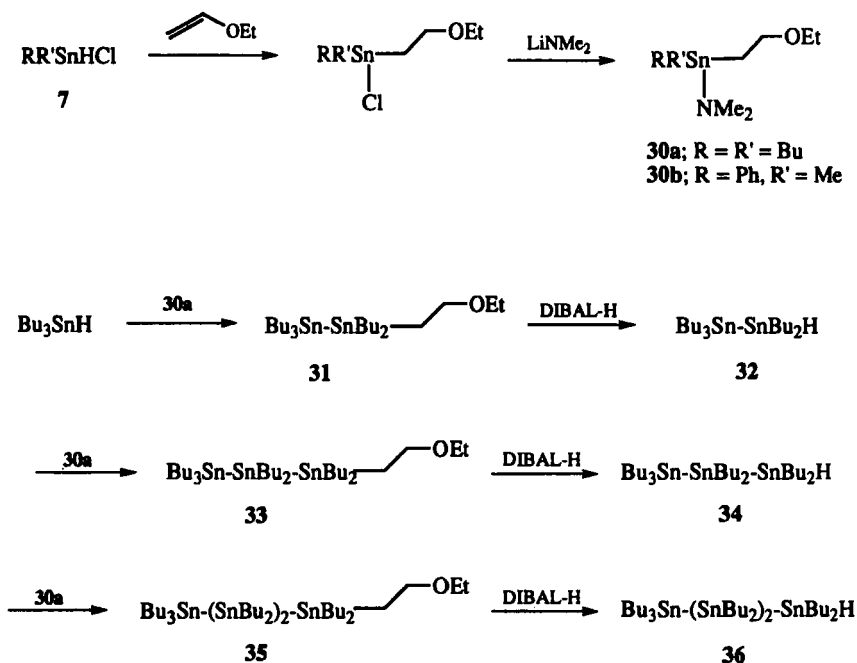
## 1. Tri- and Tetrastannanes

The synthesis of tristannanes and linear tetrastannanes can be achieved in a straightforward manner by employing the hydrostannolysis reaction and diorganotin dihydrides (**26**) and 1,1,2,2-tetraorganodistannanes (**9**) according to Eq. (8) (49). As shown, this methodology can be used to



prepare a range of compounds with a mixture of substituents, although in the case of tetrastannanes, this range is limited, since only two tetraorganodistannanes are readily available ( $\text{R} = \text{Bu}$  and  $\text{Bu}^i$  in **9**). Interestingly, the alternative reaction of diorganotin bisamides with triorganotin hydrides leads only to a mixture of oligomeric products, presumably as a result of a transamination process. A mixture of oligomeric perbutylated linear polystannanes is also obtained by the reaction of hexabutyldistannoxane (**27**) with formic acid at elevated temperature (50). From this mixture, Jousseau and co-workers (50) separated octabutytristannane (**28**) and decabutyttetrastannane (**29**) in pure form through the use of reverse-phase high-pressure liquid chromatography (HPLC). These researchers also report that the coupling of diorganotin dihydrides with triorgano(*N*-phenylformamido)stannanes, a procedure originally introduced by Creemers and Noltes (51) for the synthesis of linear polystannanes, actually produces a mixture of products as determined by HPLC analysis.

For the stepwise construction of homologously pure linear polystannane oligomers via the hydrostannolysis reaction, a new strategy that makes use of a "masked"  $\text{Sn-H}$  functional group has recently been introduced (52). As shown in Scheme 6, the reagents **30**, bearing a  $\beta$ -ethoxyethyl substituent, are prepared through the hydrostannation of ethylvinyl ether with the corresponding diorganotin hydridochloride **7**, followed by reaction of the intermediate product with lithium dimethylamide. Coupling of **30a** ( $\text{R} = \text{Bu}$ ) with tributyltin hydride provides the distannane **31**, which is treated with diisobutylaluminum hydride (DIBAL-H) to remove the



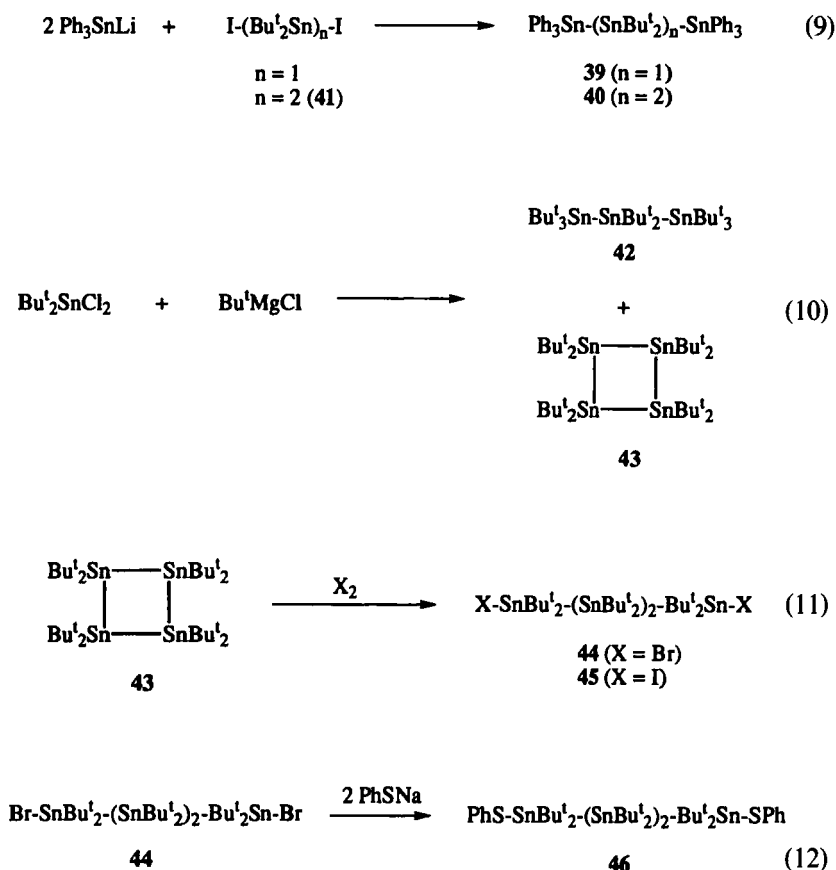
SCHEME 6

$\beta$ -ethoxyethyl group and generate the new distannane **32**. Repetition of this two-step sequence of reactions then provides the butylated tri- (**33** and **34**) and tetrastannanes (**35** and **36**). Most importantly, however, through the use of conventional column chromatography, each of the polystannanes can be purified to homogeneity, as determined by  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR and HPLC analysis, after each step in Scheme 6. Finally, by employing different coupling reagents (i.e., **30a** and **30b**), the programmed synthesis of isomeric linear polystannanes can be carried out, as in the case of the two tristannanes **37** and **38** shown in Scheme 7 (52).

In addition to the hydrostannolysis reaction, another procedure that has been used for the synthesis of tristannanes, such as compound **39**, is through the reaction of the triorganotin anions,  $\text{R}_3\text{SnLi}$ , with diorganotin dihalides according to Eq. (9) in Scheme 8. This method has also been



SCHEME 7



SCHEME 8

extended to the synthesis of the tetrastannane **40** through the addition of  $\text{Ph}_3\text{SnLi}$  to 1,2-diiodo-1,1,2,2-tetra(*t*-butyl)distannane **41** (53), as shown in Eq. (9) (54). Finally, as in the case of distannanes, a few tri- and tetrastannanes have been prepared through some novel routes. These include octa(*t*-butyl)tristannane **42**, which is obtained as a by-product in the reaction of di(*t*-butyl)tin dichloride with *t*-BuMgCl [Eq. (10), Scheme 8] (24). The main product of this latter reaction is actually the cyclotetrastannane **43** (54), which can be selectively ring-cleaved with one equivalent of either bromine or iodine to provide the 1,2-dihalo-1,1,2,2,3,3,4,4-octa(*t*-butyl)tetrastannanes **44** and **45** ( $\text{X} = \text{Br}$  and  $\text{I}$ , respectively) [Eq. (11), Scheme 8] (24,55,56). Finally, compound **44** has been used for the synthesis of the tetrastannane **46** [Eq. (12)] (24).





SCHEME 9

## 2. Higher-Order Polystannane Oligomers

Very few studies of fully characterized linear polystannanes with chain lengths of greater than four tin atoms have appeared. As mentioned previously, each of the compounds in the perethylated series,  $\text{Et}_3\text{Sn}(\text{Et}_2\text{Sn})_n\text{SnEt}_3$  ( $n = 0-4$ ) originally reported by Ceemers and Noltes (51) is likely to be a mixture of oligomeric products as revealed by modern methods of analysis. In fact, through the use of HPLC, Jousseume and co-workers (50) were also able to separate the perbutylated pentastannane,  $\text{Bu}_3\text{Sn}(\text{Bu}_2\text{Sn})_2\text{SnBu}_3$  (47), in pure form from a similar type of mixture. Extension of the synthetic methodology presented in Scheme 6 has also provided the homologously pure pentastannane and hexastannane, **48** and **49** (Scheme 9), respectively, and the potential exists for the synthesis of longer linear polystannanes by this route. Finally, using methodology presented in Scheme 8, Adams and Dräger (54) have extended their series of crystalline polystannanes to include the penta- and hexastannanes, **50** and **51**, respectively (Scheme 9).

### B. Structural Studies

Relatively few linear polystannanes have been the subject of crystallographic analysis; Table IV and Fig. 4 provide some selected structural

TABLE IV  
SELECTED BOND LENGTHS AND BOND ANGLES FOR LINEAR POLYSTANNANES

Compound	Sn-Sn (Å) <sup>a</sup>		Sn-Sn-Sn (°)	Ref.
	Sn <sub>b</sub> -Sn <sub>t</sub>	Sn <sub>b</sub> -Sn <sub>b</sub>		
$\text{Bu}^t_3\text{Sn}-\text{SnBu}^t_2-\text{SnBu}^t_3$ ( <b>42</b> )				
$\text{X}-\text{Bu}^t_2\text{Sn}-(\text{SnBu}^t_2)_2-\text{SnBu}^t_2-\text{X}$	2.966	—	122.1	(24)
X = Br ( <b>44</b> )	2.887	2.928	117.3	(24)
X = I ( <b>45</b> )	2.895	2.924	117.0	(56)
X = SPh ( <b>46</b> )	2.910	2.928	118.7	(24)

<sup>a</sup> b = bridging, t = terminal.

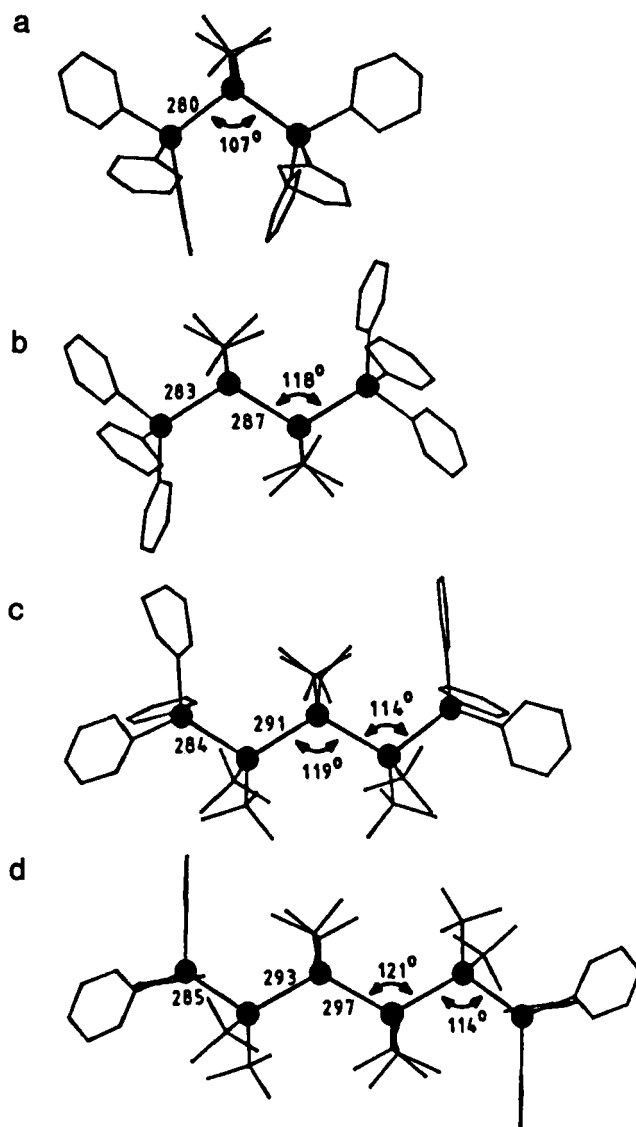


FIG. 4. Molecular structures for: (a) tristannane **39**, (b) tetrastannane **40**, (c) pentastannane **50**, and (d) hexastannane **51**. Reprinted with permission from Adams and Dräger (54).

parameters of those that have been reported to date. From this tabulation, many of the trends that were observed for substituted distannanes are preserved for the longer linear polystannanes. For instance, severe non-bonded interactions can greatly perturb both Sn-Sn bond lengths and

Sn–Sn–Sn bond angles as revealed by the solid-state structure of the tristannane **42**. In this compound, the Sn–Sn bond length has been elongated to 2.966 Å and the Sn–Sn–Sn bond angle has been opened up to an incredible 122.1° (Table IV). These values can be contrasted with the structural parameters for the tristannane **39**, which possesses more-normal Sn–Sn bond length and Sn–Sn–Sn bond angle values of 2.80 Å and 107°, respectively (Fig. 4). Compound **39** is the first in a homologous series of linear polystannanes, i.e., **39**, **40**, **50**, and **51**, that have been subjected to crystallographic analysis. As shown in Fig. 4, an interesting chain-length dependence can be observed in both the Sn–Sn bond length and the Sn–Sn–Sn bond angle values; namely, both of these structural parameters increase as the chain length gets longer. For example, in going from the tristannane **39** to the tetrastannane **40**, the  $\text{Sn}_b\text{--Sn}_b$  bond length value increases to 2.87 Å, while the Sn–Sn–Sn bond angle increases to 117.3°. Undoubtedly, these increased distortions are dictated by an increase in nonbonded interactions, and these are probably magnified further for the central tin atom as one goes to the pentastannane **50** ( $\text{Sn}_b\text{--Sn}_c$ , 2.91 Å; Sn–Sn–Sn, 119°). Quite curious, however, is the observation that the trend continues for the hexastannane **51** ( $\text{Sn}_b\text{--Sn}_c$ , 2.97 Å; Sn–Sn–Sn, 121°), even though it could be argued that the nonbonded interactions experienced for the central tin atom should have reached a maximum in **50**. Unfortunately, longer crystalline polystannanes have not yet been prepared that could be used to determine where these parameters reach their maximum values. Concerning other polystannanes, the series of tetrastannanes represented by compounds **44–46** have been studied by crystallographic analysis, and their structural parameters all fall within the range that is now expected (Table IV).

### C. Properties

#### 1. Electronic Spectroscopy

It has long been known that linear polysilane oligomers of the general formula  $\text{R}-(\text{R}_2\text{Si})_n\text{--R}$  exhibit absorption maxima that shift to longer wavelengths with an increase in chain length (57), and there has been much interest in developing theoretical models that can be used to explain the origin of this property (11,58). Polygermanes and polystannanes have also been shown to share this phenomenon. For the latter class of compounds, early work by Drenth, Noltes, and co-workers (59) showed that for the perethylated series of linear polystannanes,  $\text{Et}_3\text{Sn}(\text{Et}_2\text{Sn})_n\text{SnEt}_3$  ( $n = 0\text{--}4$ ), the lowest energy-absorption maxima red-shifted from  $\lambda_{\text{max}}$  232 nm for the distannane ( $n = 0$ ) to 325 nm for the hexastannane ( $n = 6$ ). These

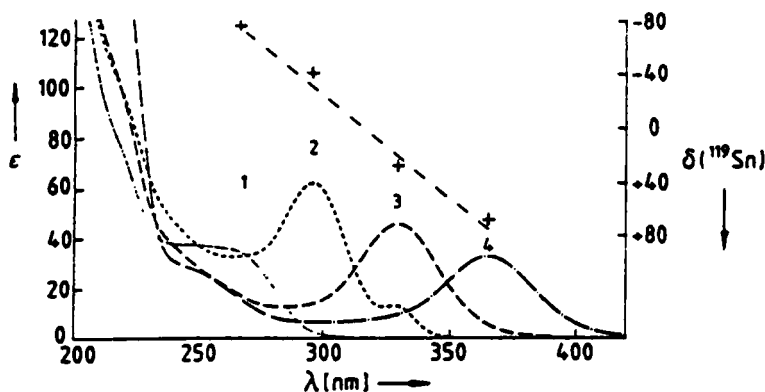


FIG. 5. Electronic spectra for: (1) tristannane **39**, (2) tetrastannane **40**, (3) pentastannane **50**, and (4) hexastannane **51**. Also shown is a plot of the  $^{119}\text{Sn}$  NMR chemical shift (ppm) of the central tin atom versus the corresponding excitation wavelength of the linear polystannane. Reprinted with permission from Adams and Dräger (54).

values are also red-shifted relative to polysilanes and polygermanes. Two other series of fully characterized linear polystannane oligomers have been spectroscopically investigated. One of these is the series of Adams and Dräger, who reported the collection of electronic spectra shown in Fig. 5 for the compounds **39**, **40**, **50**, and **51**. Once more, one observes a red-shifting of the lowest energy absorption with increasing chain length and a broadening that results in an apparent decrease in intensity for this transition. These investigators interpret the origin of this electronic property as arising from the "onset of formation of a metal-like electronic band and thus propose the term 'molecular metals' for these compounds." More recently, Takeda and Shiraishi (60) have investigated this concept through a theoretical approach, and they find that the band gap in the linear polystannane,  $\text{H}-(\text{H}_2\text{Sn})_n-\text{H}$ , should decrease significantly as a function of increasing Sn-Sn bond length and increasing Sn-Sn-Sn ( $\alpha$ ) and H-Sn-H ( $\beta$ ) bond angles. Furthermore, at fairly large values of  $\alpha$  (e.g.,  $160^\circ$ ), they suggest that a metallic state for the polystannane may exist and that this state might be stabilized by an increase in pressure.

The series of linear polystannanes represented by compounds **31**, **33**, **35**, **48**, and **49** have also been the subject of spectroscopic analysis. In this case, a similar trend is observed, although the magnitude of the red-shift per tin atom is less than that observed for the previous series (Fig. 6). This discrepancy between the two series of linear polystannanes is likely to be a result of the strong nonbonded interactions in the former (i.e., **39**, **40**, **50**, and **51**), which severely restrict conformational mobility

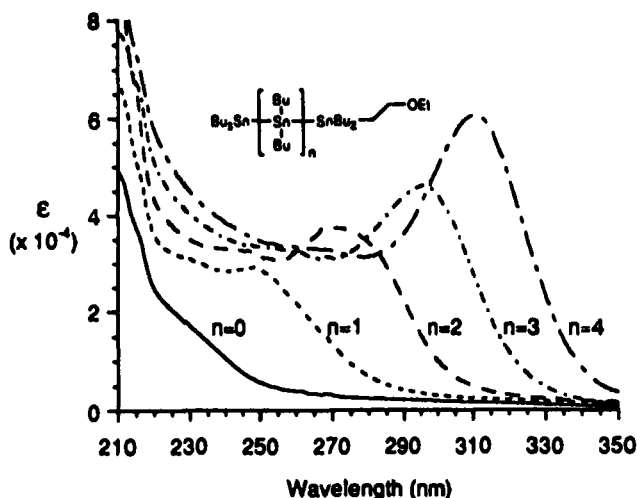


FIG. 6. Electronic spectra for the linear polystannanes represented by compound **31** ( $n = 0$ ), compound **33** ( $n = 1$ ), compound **35** ( $n = 2$ ), compound **48** ( $n = 3$ ), and compound **49** ( $n = 4$ ). Reprinted with permission from Sita (52).

and produce an increase in the mean Sn–Sn bond length with increasing chain length. For polysilanes, it has been observed that a red-shifting occurs when the Si–Si  $\sigma$ -bonded backbone adopts an all-*trans* conformation (10,11). Finally, concerning the electronic spectra of other linear polystannanes, unfortunately, only that of the tetrastannane **45** with a  $\lambda_{\max}$  of 340 nm has been reported. This absorption is shifted by nearly 50 nm relative to the tetrastannane **40**, and it will be interesting to see whether this effect of halogen substitution will be a general one. In summary, it is clear from the preceding discussion that there is still much left to be done concerning the investigation of the electronic properties of linear polystannane oligomers. In this regard, the synthesis of well-defined linear oligomers with chain lengths of greater than six tin atoms and with a variety of substituents is of paramount importance.

## 2. $^{119}\text{Sn}$ NMR Spectroscopy

The  $^{119}\text{Sn}$  NMR parameters [ $\delta$  and  $^nJ(^{119}\text{Sn}–^{119}\text{Sn})$  values] for several selected linear tri- and tetrastannanes and for one pentastannane are provided in Table V. As with distannanes, some general trends can be observed from this compilation. To begin with, an increase in the  $\alpha$ -branching of alkyl substituents has a pronounced effect on the chemical shifts of tristannanes for both the terminal and the bridging tin atoms, as seen in

TABLE V  
<sup>119</sup>Sn NMR DATA FOR SELECTED LINEAR POLYSTANNANES

Compound	$\delta$ (ppm) <sup>a</sup>		<sup>n</sup> J( <sup>119</sup> Sn <sub>b</sub> – <sup>119</sup> Sn <sub>b</sub> ) (Hz) <sup>a</sup>				Ref.
	Sn <sub>t</sub>	Sn <sub>b</sub>	<sup>1</sup> J( <sup>119</sup> Sn <sub>t</sub> – <sup>119</sup> Sn <sub>b</sub> )	<sup>1</sup> J( <sup>119</sup> Sn <sub>b</sub> – <sup>119</sup> Sn <sub>b</sub> )	<sup>2</sup> J( <sup>119</sup> Sn <sub>t</sub> – <sup>119</sup> Sn <sub>b</sub> )	<sup>3</sup> J( <sup>119</sup> Sn <sub>t</sub> – <sup>119</sup> Sn <sub>t</sub> )	
R <sub>3</sub> Sn–SnR <sub>2</sub> –SnR <sub>3</sub>							
R = Me	–99.5	–261.7	2873	—	763	—	(43b)
R = Bu (28)	–75.6	–226.6	1596	—	417	—	(50)
R = Pr <sup>i</sup>	–35.0	–132.9	403	—	188	—	(43b)
R = Bu' (42)	20.4	17.0	774 <sup>b</sup>	—	(?) <sup>c</sup>	—	(24)
X–R <sub>2</sub> Sn–(SnR <sub>2</sub> ) <sub>2</sub> –SnR <sub>2</sub> –X							
R = X = Bu (29)	–74.3	–212.6	1596	601	295	233	(48)
R = Bu', X = Br (44)	102.8	25.2	1991 <sup>b</sup>	1475 <sup>b</sup>	25	271	(24)
R = Bu', X = I (45)	67.7	17.4	2199 <sup>b</sup>	1575 <sup>b</sup>	20	307	(56)
R = Bu', X = SPh (46)	33.8	40.9	1536/1655 <sup>b</sup>	1428 <sup>b</sup>	—	250	(24)
Bu <sub>3</sub> Sn–(SnBu <sub>2</sub> ) <sub>3</sub> –SnBu <sub>3</sub> (47)	–75.6	–199 (Sn <sub>b</sub> ) –210 (Sn <sub>c</sub> )	1368	(?) <sup>c</sup>	261	220	(48)

<sup>a</sup> *b* = bridging, *t* = terminal, *c* = central.

<sup>b</sup> Might be negative in sign.

<sup>c</sup> Not reported or not observable.

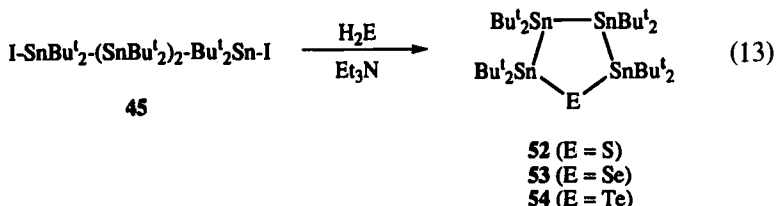
going from  $R = \text{Me}$  to  $R = \text{Bu}'$ . In this series, the chemical shift for the bridging tin atom moves over a remarkably large range by shifting from a value of  $-261.7$  ppm to a value of  $17.0$  ppm. For the first three members of this series (i.e.,  $R = \text{Me}$ ,  $\text{Bu}$ , and  $\text{Pr}'$ ), a steady decrease in the  ${}^nJ(^{119}\text{Sn}-^{119}\text{Sn})$  ( $n = 1$  and  $2$ ) values is also observed. This latter trend is surprisingly broken, however, by a jump in magnitude for  ${}^1J(^{119}\text{Sn}-^{119}\text{Sn})$  that is observed for the case where  $R = \text{Bu}'$  (Table V). In this regard, it is important to mention that what are reported in Table 5 are actually the absolute magnitudes for the coupling constants,  $|{}^nJ(^{119}\text{Sn}-^{119}\text{Sn})|$ . Since it has been previously shown that  ${}^1J(^{119}\text{Sn}-^{119}\text{Sn})$  values can be negative in sign and that a change in sign from positive to negative occurs around a Sn-Sn bond length of  $2.85 \text{ \AA}$ , the value reported for  $R = \text{Bu}'$  (Sn-Sn,  $2.966 \text{ \AA}$ ) might, in fact, be a negative value (44a,54). If this correction is made, then the original trend observed for the series is preserved.

In comparing the values of  ${}^nJ(^{119}\text{Sn}-^{119}\text{Sn})$  reported for the perbutylated polystannane series,  $\text{Bu}_3\text{Sn}-(\text{Bu}_2\text{Sn})_n-\text{SnBu}_3$  ( $n = 1-3$ ) (compounds **28**, **29**, and **47**), it is interesting to note the chain-length dependence of the  ${}^1J(^{119}\text{Sn}_i-^{119}\text{Sn}_b)$  values, which decrease from a value of  $2873 \text{ Hz}$  to a value of  $1368 \text{ Hz}$  as  $n$  goes from 1 to 3 (Table V). It is difficult to imagine that for  $R = \text{Bu}$  there is a significant change in the  $\text{Sn}_i-\text{Sn}_b$  bond length for the series of compounds. Thus, it seems probable that the  ${}^1J(^{119}\text{Sn}_i-^{119}\text{Sn}_b)$  values for these compounds are reflecting a subtle change in the electronic structure of the polystannane backbone as chain length increases. Another interesting observation can be made by comparing the  ${}^nJ(^{119}\text{Sn}-^{119}\text{Sn})$  values obtained for the series of tetrastannanes listed in Table V. In this comparison, it is interesting to note that the  ${}^1J(^{119}\text{Sn}-^{119}\text{Sn})$  values appear to be significantly enhanced for the compounds **44-46** relative to those of the perbutylated compound **47**. However, all of the Sn-Sn bonds for **44-46** are over  $2.85 \text{ \AA}$ ; therefore, it is possible that the values of  ${}^1J(^{119}\text{Sn}-^{119}\text{Sn})$  that are reported for these compounds should be negative as well. As mentioned previously, a detailed understanding of all of these phenomenon awaits the synthesis of additional linear polystannanes derivatives.

#### D. Reactivity

Much less has been documented concerning the chemical reactivity of linear polystannane oligomers, but, at the outset, it can be expected to closely parallel that reported for distannanes. It is known that these compounds are air-sensitive when the substituents possess small steric bulk. But so far, no attempts have been conveyed concerning the controlled

oxidation or insertion of sulfur and selenium into the Sn–Sn bonds of these compounds. In the absence of disproportionation, this latter reaction might lead to oligomers of the general formula  $R_3Sn-(R_2SnE)_n-SnR_3$  ( $E = S$  and  $Se$ ), which might possess interesting properties (61). Linear polystannanes are known to undergo photolytic Sn–Sn bond dissociation; however, a detailed investigation of their thermal stability has yet to be conducted (62). Finally, the 1,4-diiodotetra-stannane **45** has found utility as a precursor to the cyclic compounds **52–54** via the route shown in Eq. (13) (63).



#### IV

### BRANCHED POLYSTANNANES

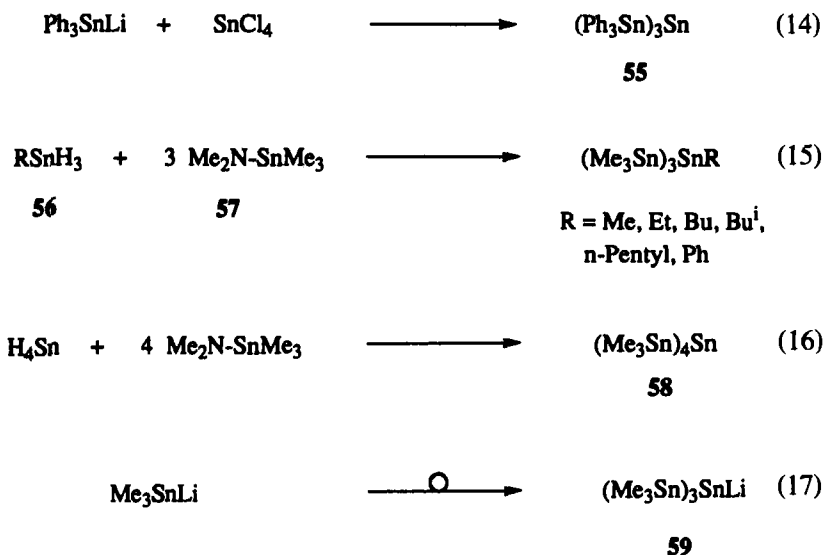
#### A. Synthesis

The first synthesis of a branched polystannane was achieved by Willemssens and van der Kerk (64) through the reaction of  $\text{Ph}_3\text{SnLi}$  with tin tetrachloride to produce compound **55**, as shown in Scheme 10 [Eq. (14)]. A more general route, however, is represented by the hydrostannolysis reaction between organotin trihydrides **56** and (dimethylamino)trimethylstannane (**57**) according to Eq. (15) (65). In fact, extension of this methodology was also successfully used to prepare the permethylpentastannane **58** [Eq. (16)] (65). Finally, it has been shown that a solution of  $\text{Me}_3\text{SnLi}$  disproportionates to produce  $(\text{Me}_3\text{Sn})_3\text{SnLi}$  (**59**) in solution [Eq. (17)] (44c,66), and this compound has in turn been used to prepare branched polystannane transition-metal complexes (67).

#### B. Structural Studies, Properties, and Reactivity

Unfortunately, very little has been done to date regarding the investigation of branched polystannanes. No structural studies have been performed, and only the electronic spectrum of compound **55** ( $\lambda_{\text{max}}$  277 nm;





SCHEME 10

$\epsilon_{\text{max}}$  79,000) has been reported (37). Most of the compounds shown in Scheme 10 have, however, been the subject of investigation by  $^{119}\text{Sn}$  NMR spectroscopy; the data collected from these studies are listed in Table VI. As can be seen in this compilation, an increase in the number of tin atoms bonded to the tin center dramatically alters its chemical shift to higher field [*cf.*  $\delta$  -108.1 ppm for  $\text{Me}_3\text{SnSnMe}_3$ , -261.7 ppm for  $(\text{Me}_3\text{Sn})_2\text{SnMe}_2$ , -489.7 ppm for  $(\text{Me}_3\text{Sn})_3\text{SnMe}$ , and -739 ppm for  $(\text{Me}_3\text{Sn})_4\text{Sn}$ ]. Another feature is that as more tin atoms are bonded to the central tin, the  $^1J(^{119}\text{Sn}-^{119}\text{Sn})$  values progressively decrease in magnitude [*cf.* 4404 Hz for  $\text{Me}_3\text{SnSnMe}_3$ , 2873 ppm for  $(\text{Me}_3\text{Sn})_2\text{SnMe}_2$ , 1733 Hz for  $(\text{Me}_3\text{Sn})_3\text{SnMe}$ , and 881 Hz for  $(\text{Me}_3\text{Sn})_4\text{Sn}$ ]. A similar relationship is also observed for the  $^2J(^{119}\text{Sn}-^{119}\text{Sn})$  values (Table VI). Since structural parameters for these compounds do not yet exist, it is not clear whether some of the trends can be attributed to an increase in Sn-Sn bond lengths as the degree of branching at the central tin atom increases. It is likely, however, that the effective nuclear charge at the central tin atom,  $Z_{\text{eff}}$ , does vary with branching, and this then may be involved, at least to some degree, in defining the  $^{119}\text{Sn}$  spectral parameters. Finally, while the chemical reactivity of branched polystannanes has not been investigated, Mitchell and El-Behairy (65) do report that heating a solution of  $(\text{Me}_3\text{Sn})_3\text{SnMe}$  in benzene at 80°C resulted in decomposition to produce hexamethyldistannane and some as-yet-unidentified products.

TABLE VI  
 $^{119}\text{Sn}$  NMR DATA FOR BRANCHED POLYSTANNANES

Compound	$\delta$ (ppm) <sup>a</sup>		$^nJ(^{119}\text{Sn}_b-^{119}\text{Sn}_b)$ (Hz) <sup>a</sup>		Ref.
	$\text{Sn}_t$	$\text{Sn}_b$	$^1J(^{119}\text{Sn}_t-^{119}\text{Sn}_b)$	$^2J(^{119}\text{Sn}_t-^{119}\text{Sn}_t)$	
$\text{RSn}(\text{SnMe}_3)_3$					
R = Me	-89.5	-489.7	1733	287	(65)
R = Et	-89.3	-440.9	1538	259	(65)
R = Bu	-90.3	-459.9	1548	265	(65)
R = Bu <sup>i</sup>	-90.3	-480.4	1546	262	(65)
R = n-Pentyl	-90.1	-460.5	1535	262	(65)
R = Ph	-83.2	-434.2	1670	271	(65)
R = Li ( <b>59</b> )	-101.7	-1044	-5737	908	(44a-c)
$\text{Sn}(\text{SnMe}_3)_4$ ( <b>58</b> )	-80.0	-739.0	881	20	(44a-c)

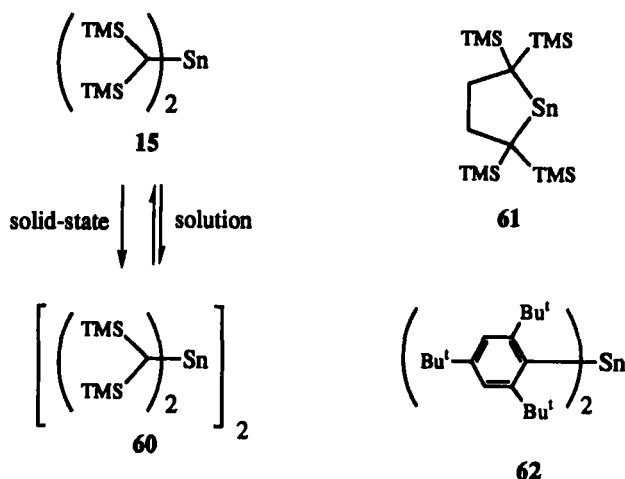
<sup>a</sup> b = bridging, t = terminal.

## V

### CYCLOPOLYSTANNANES

#### A. Synthesis

Of all the different structural classes for polystannanes, cyclic structures have received by far the most attention. Much of this interest emanates from early reports claiming the successful synthesis of monomeric divalent diorganotin species (stannylenes) of the general formula  $\text{R}_2\text{Sn}$  for the specific cases of R = cyclohexyl and phenyl (68). Subsequent investigations have proven, however, that only through the use of organic substituents that are extremely sterically encumbered can one stabilize the monomeric form. This concept was demonstrated by the classical work of Lappert and co-workers (25,69), who synthesized compound **15** and found that, while dimeric in the solid state in the form of the distannene **60**, it was present in solution to a large extent as the monomer (Scheme 11). This solution equilibrium between stannylene and distannene was later confirmed by variable-temperature NMR and ultraviolet (UV) spectroscopic studies (23,70). By fine-tuning the steric envelope surrounding the tin atom, Sakurai and co-workers (71) recently succeeded in synthesizing the first divalent diorganotin compound, compound **61**, which is monomeric both in solution and in the solid state, as revealed by crystallographic analysis. The molecular structure of **61** as provided by this latter study is shown in Fig. 7. Finally, Weidenbruch and co-workers (72) were also



SCHEME 11

subsequently able to show that the diarylstannylene **62** is monomeric in solution and the solid state (Scheme 11).

Regarding cyclopolystannanes, it was first proposed by Neumann and König (73) that the "diphenyltin," which was previously prepared from either reduction of diphenyltin dichloride with alkaline metals or reaction of tin dichloride with either phenyllithium or phenylmagnesium bromide, was, in fact, dodecaphenylcyclohexastannane **63** (Scheme 12). This was later confirmed by the partial structural analysis of **63**, which revealed the tin atoms to be arranged in a six-membered ring that adopts a chair conformation (74). Neumann and König also determined that **63** could be produced through the pyridine-catalysed dehydrogenative coupling of diphenyltin dihydride according to Scheme 12. Through extension of this latter methodology, Neumann and co-workers (75) reported the synthesis of a number of other peraryl cyclohexastannanes, as well as the synthesis of a number of peralkyl cyclopolystannanes,  $(\text{R}_2\text{Sn})_n$ , of varying ring sizes. For example, where R = ethyl, cyclopolystannanes for  $n = 6$  and 9 are supposedly formed. Additional cyclic compounds reported by this group include a cyclotetrastannane for R = benzyl and a cyclopentastannane for R = cyclohexyl. Furthermore, by varying the nature of the amine used for the dehydrogenative coupling reaction, it was claimed that decaphenylcyclopentastannane could be formed. Subsequent reinvestigations have now revealed by crystallographic analysis that dodecabenzylcyclohexastannane **64** is formed as the major product under the conditions reported for the synthesis of the cyclotetrastannane (Scheme 12) (76), and

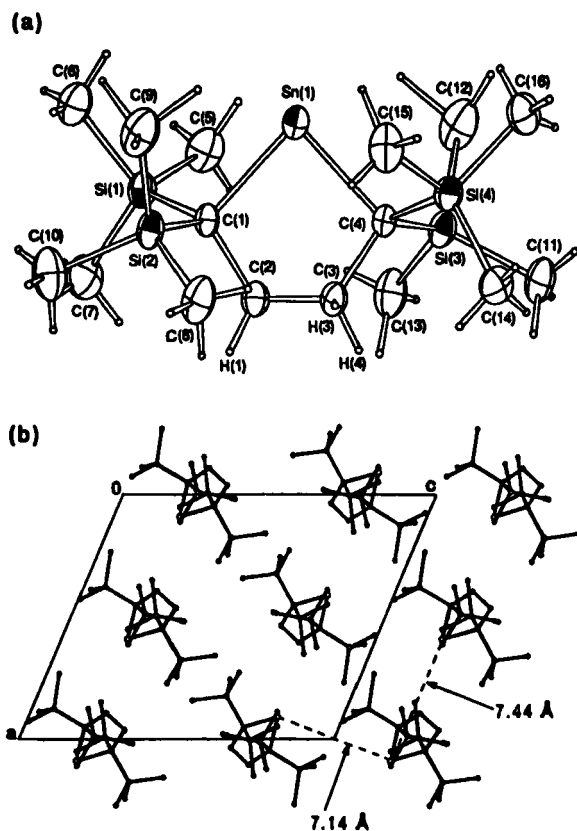
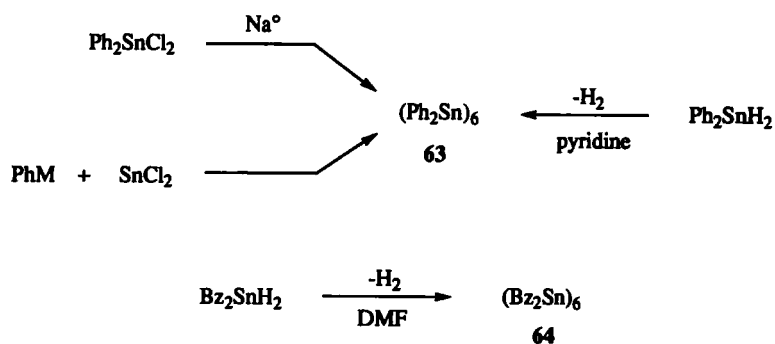
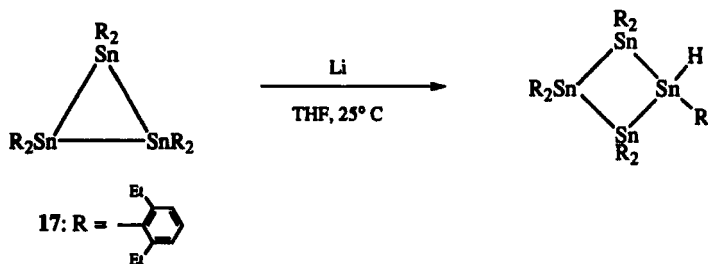
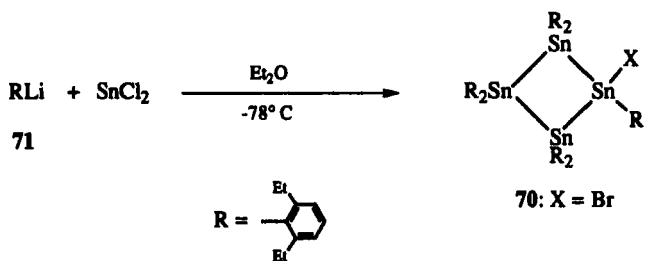
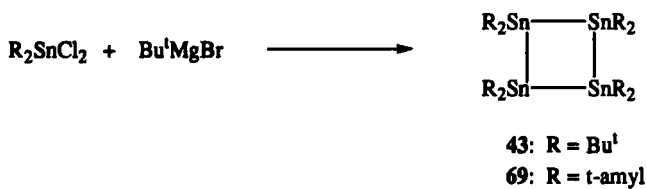
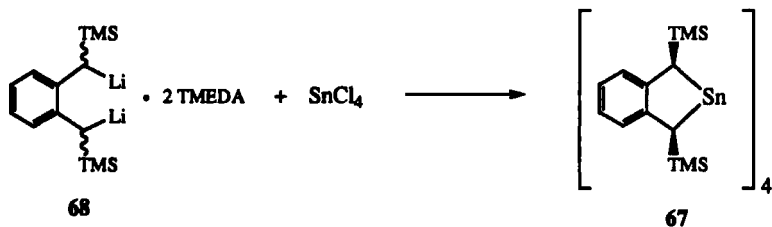
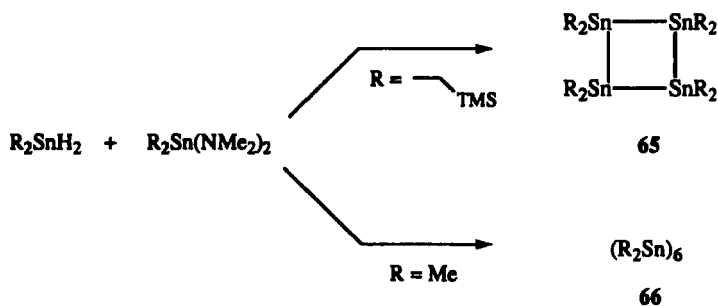


FIG. 7. Molecular structure of the stannylene **61**. Reprinted with permission from Kira *et al.* (71).



M = Li or MgBr; Bz = benzyl; DMF = dimethylformamide

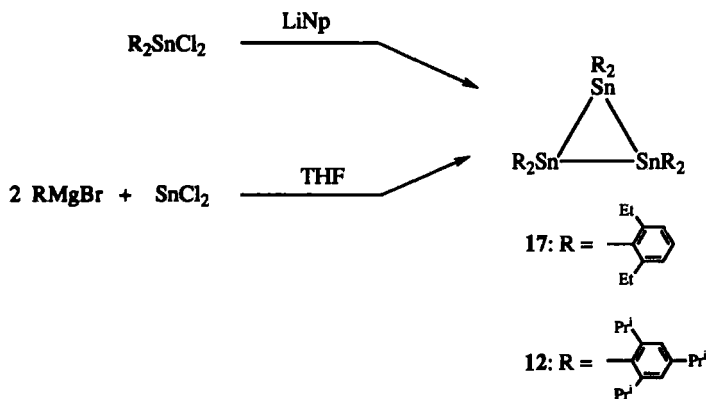
SCHEME 12



SCHEME 13

the cyclohexastannane **63** is still the major product when the original synthesis of decaphenylcyclopentastannane is carried out (77). To date, unequivocal determination of the structure reported for decacyclohexylcyclopentastannane by either crystallographic analysis or  $^{119}\text{Sn}$  NMR spectroscopy has not been reported. However, Jousseau and co-workers (78) have recently used this latter technique to verify the structures of decabutylcyclopentastannane,  $(\text{Bu}_2\text{Sn})_5$ , and dodecabutylcyclohexastannane,  $(\text{Bu}_2\text{Sn})_6$ , both of which were isolated in pure form from a mixture of cyclopolystannanes prepared from the palladium-catalyzed dehydrogenative cyclization of dibutylstannane.

In addition to the methods shown in Scheme 12 for the synthesis of cyclopolystannanes, this class of compound has been prepared by a hydrostannolysis procedure that utilizes diorganotin dihydrides and diorganotin bisamides. In this way, the cyclotetrastannane **65** was prepared in high yield according to Scheme 13 (79). This strategy has also been used to prepare dodecamethylcyclohexastannane **66** as well as its perdeuterated analog (80). For the synthesis of other cyclotetrastannanes, Lappert and co-workers (81) isolated the four-membered ring compound **67** through reaction of tin tetrachloride with the organolithium reagent **68** at  $-78^\circ\text{C}$  (Scheme 13). In addition, Puff and co-workers (53) utilized the same procedure as for the synthesis of octa-*t*-butylcyclotetrastannane **43** to prepare the cyclotetrastannane **69** that possesses *t*-amyl (i.e., 1,1-dimethylpropyl) substituents. The cyclotetrastannane **70** bearing one bromine substituent was produced unexpectedly from the reaction of 1-lithio-2,6-diethylbenzene **71** with tin dichloride at  $-78^\circ\text{C}$  in diethyl ether (82). Finally, it has been reported that the reaction of a solution of the cyclotristannane **17** in THF with lithium metal, followed by quenching with ammonium



SCHEME 14

chloride, results in a very good yield of the substitutionally unsaturated cyclotetrastannane (see Scheme 13) (39).

Concerning the synthesis of the smallest cyclopolystannane ring system, the first synthesis of a cyclotristannane was achieved in 1983 through the reduction of bis(2,6-diethylphenyl)tin dichloride with lithium naphthalenide at low temperature according to Scheme 14 (27). The cyclotristannane **12** was prepared in a similar fashion a few years later (21). Since then, several groups have reported that these cyclotristannanes can be prepared in a straightforward fashion through addition of the corresponding aryl-magnesium bromide reagents to a solution of tin dichloride in tetrahydrofuran (83–85). Paralleling these observations, it has also been reported that the synthesis of the cyclopolystannanes,  $(\text{Phen}_2\text{Sn})_n$  ( $n = 3, 4$ , and  $6$ ) (Phen = 9-phenanthryl) can be achieved via similar procedures (86).

### B. Structural Studies

Dodecaphenylcyclohexastannane **63** has been the subject of several crystallographic analyses (74,76,77). Surprisingly, as Table VII reveals, the structural parameters for this compound, such as Sn–Sn bond lengths and Sn–Sn–Sn bond angles, are remarkably dependent on its crystalline form. Thus, without inclusion of solvent molecules in the unit cell, **63** adopts a conformation with Sn–Sn–Sn bond angles ranging from  $108.3^\circ$  to a very wide value of  $121.6^\circ$ , whereas when two molecules of toluene are included, these bond angles are in the more expected range of  $109.5^\circ$  to  $114.0^\circ$ . In the latter structure, the Sn–Sn bonds are also slightly reduced to  $2.775 \text{ \AA}$  from the  $2.781 \text{ \AA}$  value observed for the former crystalline form. Altogether, this structural information supports the view that due to small-force constants for Sn–Sn bond length and Sn–Sn–Sn bond angle

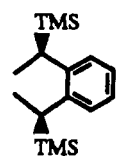
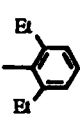
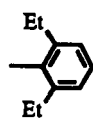
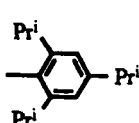
TABLE VII  
SELECTED BOND LENGTHS AND BOND ANGLES  
FOR  $[\text{Ph}_2\text{Sn}]_6$  (**63**) (76,77)

Parameter	Crystal Form		
	A	B	2 toluene
Sn–Sn bond lengths ( $\text{\AA}$ )	2.781	2.787	2.775
Sn–Sn–Sn bond angles ( $^\circ$ )			
Sn1–Sn2–Sn3	108.3	109.0	109.5
Sn2–Sn3–Sn(1')	121.6	107.4	114.0
Sn3–Sn(1')–Sn(2')	111.7	116.0	113.9

distortions, the equilibrium geometry of polystannane frameworks are easily perturbed by both internal forces (e.g., nonbonded interactions) and external forces (e.g., crystal packing). The crystal structure of dodecabenzylcyclohexastannane **64** reveals very few surprises, with a mean Sn–Sn bond length of 2.802 Å and Sn–Sn–Sn bond angles in the range 105°–111.7° (76).

Forced to adopt formal bond angles of 60° and 90° degrees, respectively, the skeletal frameworks of cyclotristannanes and cyclotetrastannanes are of interest with regard to the information they could provide concerning the origins and manifestations of strain in polystannane structures. The

TABLE VIII  
SELECTED BOND LENGTHS AND BOND ANGLES FOR CYCLOTETRASTANNANES  
AND CYCLOTRISTANNANES

Compound	Sn–Sn (Å)	Sn–Sn–Sn (°)	Ring	Ref.
$[R_2Sn]_4$				
R = Bu' ( <b>43</b> )	2.887	90	Planar	(53)
R = <i>t</i> -amyl ( <b>69</b> )	2.919	89.1	Puckered	(53)
$R_2 = $  ( <b>67</b> )	2.852	88.2	Planar	(81)
R = trimethylsilylmethyl ( <b>65</b> )	2.831	90	Planar	(79)
BrSnR[SnR <sub>2</sub> ] <sub>3</sub> ( <b>70</b> )				
$R = $ 	2.899			
	2.910		Puckered	(82)
	2.843			
	2.831			
$[R_2Sn]_3$				
$R = $  ( <b>17</b> )	2.854			
	2.856	60 (avg)	Isocoles	(27)
	2.870			
$R = $  ( <b>12</b> )	2.916	60.16		
	2.947	60.73	Scalene	(84)
	2.963	59.13		



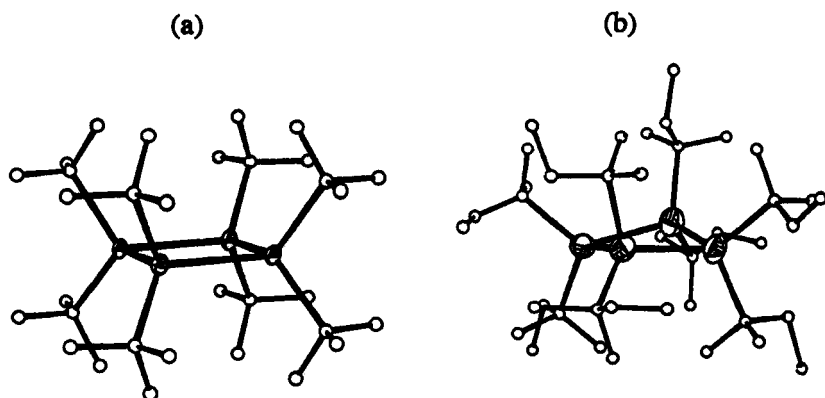


FIG. 8. Molecular structures of: (a) the cyclotetrastannane **43**, and (b) the cyclotetrastannane **69**. Reprinted with permission from Puff *et al.* (53).

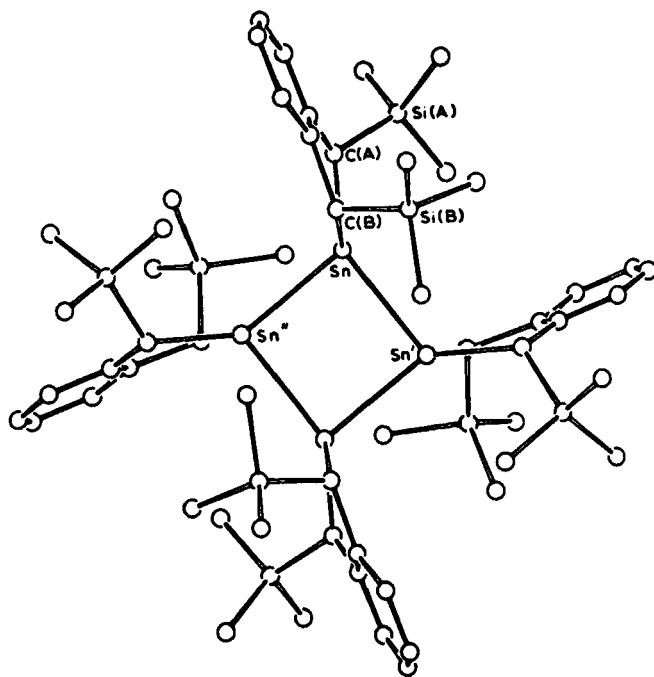


FIG. 9. Molecular structure of the cyclotetrastannane **67**. Reprinted with permission from Lappert *et al.* (81).

first cyclotetrastannane to be structurally characterized was the *t*-butylated derivative **43**, and this compound was subsequently subjected to full crystallographic analysis along with the cyclotetrastannane **69** (53). As Table VIII and Fig. 8 indicate, the two cyclotetrastannanes adopt different ring conformations, with **43** being planar and **69** being puckered. The mean Sn–Sn bond length of the latter, 2.919 Å, is slightly longer than the 2.887 Å found for **43**.

A very interesting cyclotetrastannane structure is that of compound **67** reported by Lappert and co-workers (81). During the synthesis of this cyclotetrastannane, several different diastereomers could have been formed; however, only the diastereomer shown in Fig. 9 of  $C_{4h}$  symmetry was produced. The four-membered ring in this structure is planar, with a Sn–Sn bond length of 2.852 Å and a mean Sn–Sn–Sn bond angle of 88.2°. Another planar cyclotetrastannane is compound **65**, which has a slightly shorter mean Sn–Sn bond length, 2.831 Å (Table VIII) (79). Finally, Cardin and co-workers (82) have reported the structure of the novel bromocyclotetrastannane **70**, which adopts a substantially puckered conformation in the solid state. In addition, most of the Sn–Sn–Sn bond angles in this structure deviate significantly from 90°, and the Sn–Sn bond

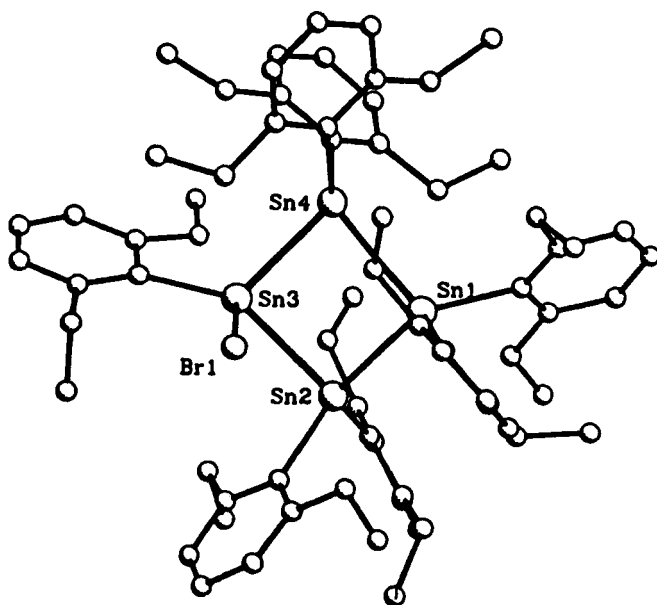


FIG. 10. Molecular structure of the cyclotetrastannane **70**. Reprinted with permission from Cardin *et al.* (82).

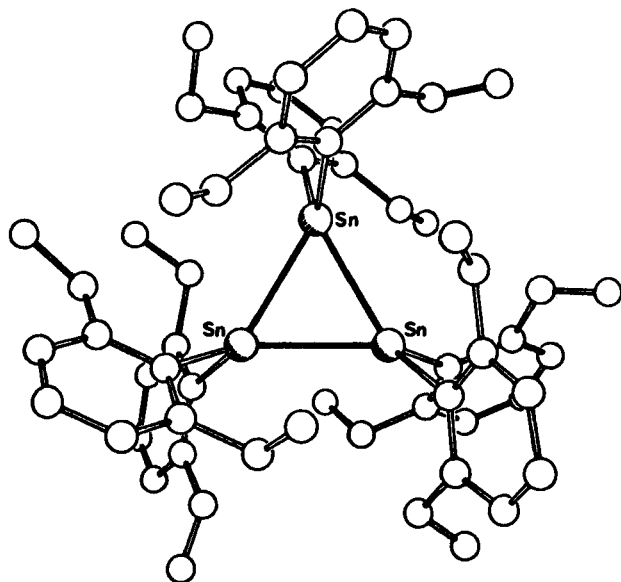


FIG. 11. Molecular structure of the cyclotristannane **17**. Reprinted with permission from Masamune *et al.* (27).

lengths fall into two categories, long and short, as Table VIII and Fig. 10 reveal.

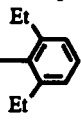
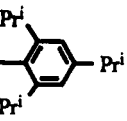
Concerning cyclotristannanes, both the derivatives **17** and **12** have been the subjects of crystallographic analysis. As shown in Fig. 11, compound **17** forms an isosceles triangle in the solid state, with Sn–Sn bond lengths of 2.854, 2.856, and 2.870 Å, respectively (Table 8) (27). However, this distortion from the expected equilateral structure produces very minor deviations in the observed Sn–Sn–Sn bond angles. Several years after its synthesis was first reported, the crystal structure of the more sterically encumbered cyclotristannane **12** was also determined (84). Although the refinement for this preliminary structure is less than optimal, owing to the large size and complexity of the unit cell, several important features can still be discerned. First, the Sn–Sn bond lengths for **12** form a scalene triangle, with distinct values of 2.916, 2.947, and 2.963 Å, respectively. Most importantly, due to severe nonbonded steric interactions present in this compound, the planes defined by the Sn<sub>3</sub> ring and the C–Sn–C bond angles deviate from orthogonality by between 8.1° and 11.5°. It is likely that this pronounced structural distortion is responsible for the low barrier to Sn–Sn bond dissociation present in the molecule (see later).

## C. Properties

The electronic spectrum of dodecaphenylcyclohexastannane **63** exhibits an intense absorption maximum at  $\lambda_{\max}$  280 nm ( $\epsilon_{\max} \sim 45,000$ ). In the two cyclotristannanes, this characteristic feature is shifted to longer wavelengths and now appears at  $\lambda_{\max}$  295 nm ( $\epsilon_{\max}$  45,000) for **17** and at  $\lambda_{\max}$  300 nm ( $\epsilon_{\max}$  55,000) for **17** (21,27). Whether this shift is a result of longer Sn–Sn bond lengths in the three-membered ring system or is an inherent property of the cyclotristannane framework itself remains a question until further studies with these compounds are performed. In this regard, it is unfortunate that the electronic spectra of other cyclopolystannanes have not been reported.

As Table IX reveals, a number of cyclopolystannanes have been subjected to analysis by  $^{119}\text{Sn}$  NMR spectroscopy. For these compounds, the values for the various  $^nJ(^{119}\text{Sn}–^{117}\text{Sn})$  coupling constants can be unequivocally established via the relationship of the relative intensities of the satel-

TABLE IX  
 $^{119}\text{Sn}$  NMR DATA FOR SELECTED CYCLOPOLYSTANNANES

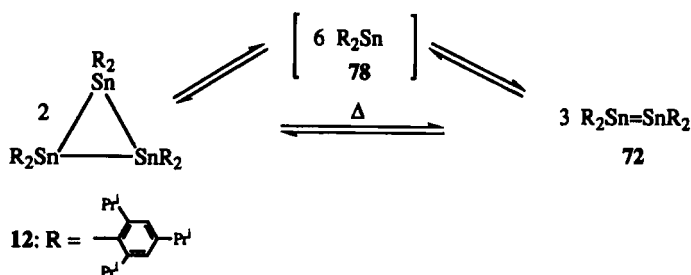
Compound	$\delta$ (ppm)	$^nJ(^{119}\text{Sn}–^{117}\text{Sn})$ (Hz)			Ref.
		$^1J(^{119}\text{Sn}–^{117}\text{Sn})$	$^2J(^{119}\text{Sn}–^{117}\text{Sn})$	$^3J(^{119}\text{Sn}–^{117}\text{Sn})$	
$[\text{R}_2\text{Sn}]_6$					
R = Ph ( <b>63</b> )	–208	1117	813	71	(77)
R = Bz ( <b>64</b> )	–140	769	362	(?) <sup>a</sup>	(76)
R = Bu	–202	462	386	81	(78)
$[\text{R}_2\text{Sn}]_5$					
R = Bu	–201	476	461	—	(78)
$[\text{R}_2\text{Sn}]_4$					
R = Bu' ( <b>43</b> )	99	1195	1658	—	(53)
R = <i>t</i> -amyl ( <b>69</b> )	101	1339	1573	—	(53)
R = trimethylsilylmethyl ( <b>65</b> )	–77	624	3850	—	(21)
$[\text{R}_2\text{Sn}]_3$					
R =  (17)	–416	2285	—	—	(26)
R =  (12)	–379	3017	—	—	(20)

<sup>a</sup> Not observed or not reported.

lites to the main resonance. In fact, as long as one is observing all the coupling constants that are possible,  $^{119}\text{Sn}$  NMR spectroscopy is a powerful tool for establishing the ring size of cyclopolystannanes. For cyclohexastannanes, the absolute magnitudes for the  $^nJ(^{119}\text{Sn}-^{117}\text{Sn})$  constants fall off with increasing  $n$ . However, for cyclotetrastannanes, it is curious to note that the two-bond coupling constant,  $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ , is routinely larger than the corresponding one-bond coupling constant,  $^1J(^{119}\text{Sn}-^{117}\text{Sn})$ . One possible explanation for this trend is that for cyclotetrastannanes, the two two-bond pathways both make positive additive contributions to the value of  $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ . Finally, it is interesting to note that for both of the cyclotristannanes, **17** and **12**, the values for  $^1J(^{119}\text{Sn}-^{117}\text{Sn})$  fall within the range expected for simple compounds such as distannanes.

Perhaps the most important question concerning the properties of cyclopolystannanes is in regard to their thermodynamic stability. In the case of cyclohexastannanes, it can be anticipated that the six-membered rings in these compounds are relatively ring-strain free, and therefore they should be thermodynamically stable. For compounds **63** and **64**, this assumption appears to be valid. However, for dodecamethylcyclohexastannane **66**, it has been reported that this compound undergoes facile disproportionation in solution at room temperature to produce an equilibrium mixture of **66** and the corresponding five-, seven-, and eight-membered cyclopolystannanes, as suggested by  $^{119}\text{Sn}$  NMR spectroscopy (80). In this particular case, it is possible that the methyl substituents cannot provide the minimum steric barrier required to prevent the bimolecular interactions that may be responsible for initiating disproportionation.

Regarding the three- and four-membered rings of cyclotristannanes and cyclotetrastannanes, it is interesting to note that the cyclotetrastannane **43** is apparently thermally robust in solution to temperatures of at least  $100^\circ\text{C}$  while there is evidence to suggest that the cyclotristannane **17** begins to disproportionate in solution above  $80^\circ\text{C}$ . This difference in stability is in keeping with recent theoretical calculations that predict that, in contrast to cyclopropane and cyclobutane, which possess similar strain-energy (SE) values, the parent cyclotristannane,  $(\text{H}_2\text{Sn})_3$ , is considerably more strained ( $\text{SE} = 36.6 \text{ kcal mol}^{-1}$ ) than the parent cyclotetrastannane,  $(\text{H}_2\text{Sn})_4$  ( $\text{SE} = 12.2 \text{ kcal mol}^{-1}$ ) as a result of a greater reluctance of the heavier Group 14 elements to engage in the  $sp$  hybridization that is required for the formation of three-membered rings (87,88). With the cyclotristannane **12**, the barriers to disproportionation have now been lowered to the extent that this process occurs readily at room temperature (21). In this system, it has been unequivocally established that **12** is in rapid thermal equilibrium with the distannene **72**, according to Scheme 15 as supported by both variable-temperature UV spectroscopy (Fig. 12) and  $^{119}\text{Sn}$  NMR spectroscopy. Through this latter method, it was also established that



SCHEME 15

compound **12** can be converted quantitatively to the distannene **72** through photolysis at  $-78^\circ\text{C}$ .

#### D. Reactivity

Depending on the steric bulk of the substituents, cyclopolystannanes are stable towards air oxidation to varying degrees. Thus, whereas dodecamethylcyclohexastannane **66** oxidizes almost spontaneously, the dodeca-

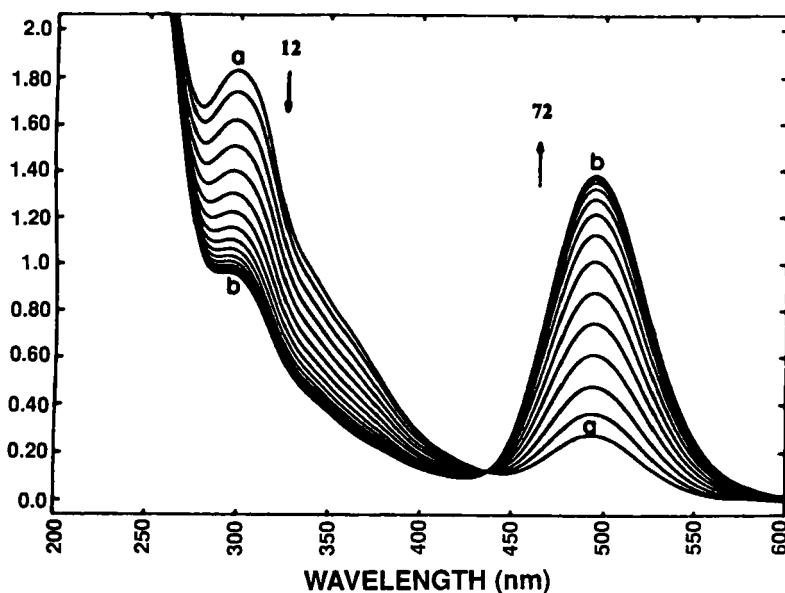
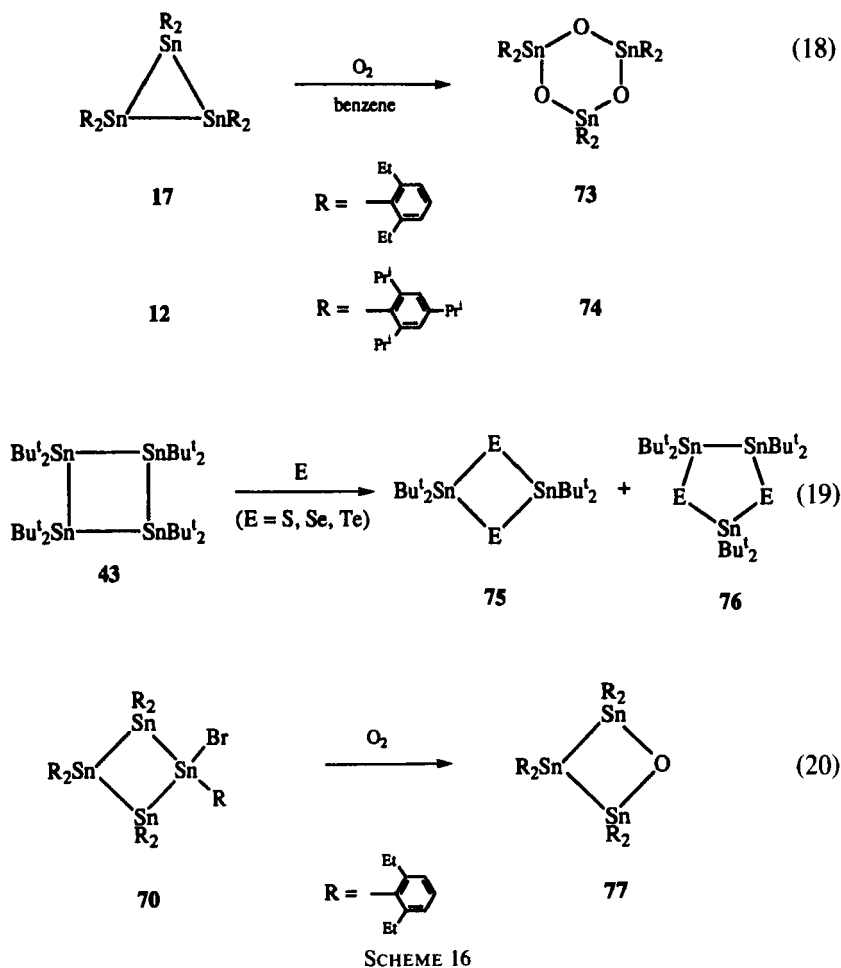
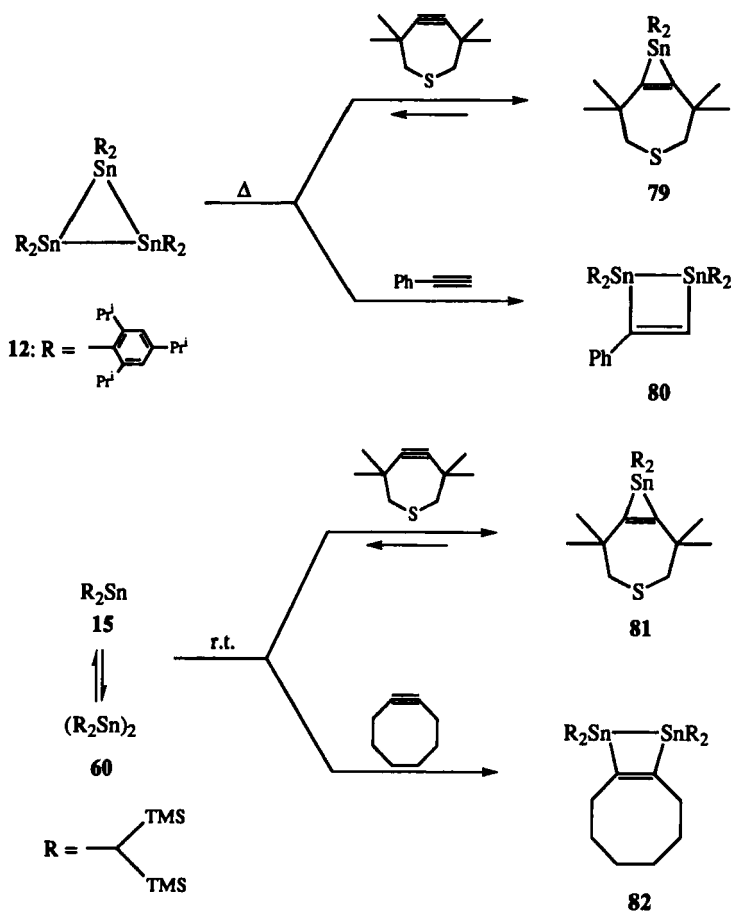


FIG. 12. Electronic spectra showing the conversion of the cyclopolystannane **12** to the distannene **72**. Trace (a) is the spectrum taken after near thermal equilibrium of the cell at room temperature, and trace (b) is the spectrum taken after near thermal equilibrium of the cell at  $90^\circ\text{C}$ . Spectra taken every 2 seconds. Reprinted with permission from Masamune and Sita (21).



phenyl derivative **63** appears to be indefinitely stable in both solution and the solid state. Except for compound **70**, all of the cyclotetrastannanes reported to date also appear to be stable towards air oxidation as well as the cyclotristannanes, **17** and **12**, in solid form. However, in solution, these latter two compounds slowly oxidize to the corresponding cyclotrisstannoxanes **73** and **74**, respectively, which have been structurally characterized [Eq. (18), Scheme 16] (21,27). With other chalcogens (S, Se, and Te), Puff and co-workers (89) were able to isolate the new compounds **75** and **76** starting from the cyclotetrastannane **43** according to Eq. (19). Interestingly, the product of a chalcogen atom inserting into a single Sn–Sn

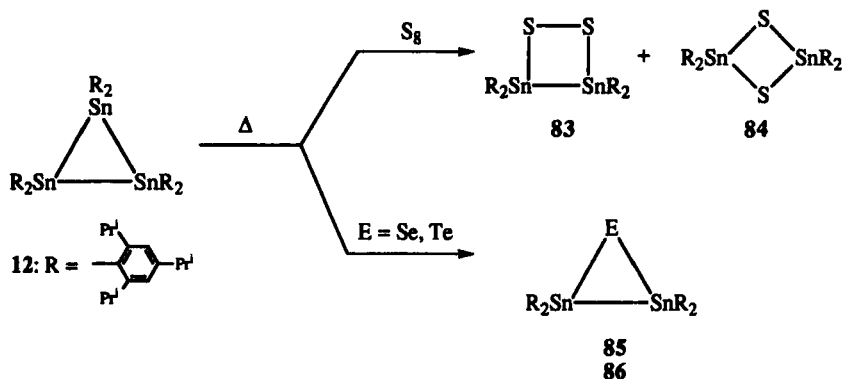


SCHEME 17

bond of **43** [i.e., compounds **52–54**, Eq. (13)] could not be observed. Finally, it has been observed that the cyclotetrastannane **70** oxidizes in solution to produce the new four-membered ring compound **77**, which has been structurally characterized [Eq. (20)] (90).

As noted earlier, the cyclotristannane **12** is a good thermal source for the distannene **72**, and presumably also for the diarylstannylene **78**,  $R_2Sn$  ( $R = 2,4,6\text{-triisopropylphenyl}$ ), which is not spectroscopically observed but which must be involved in the equilibrium between **12** and **72**. Given this, several groups have employed **12** as a precursor to **72** and **78** in order to study their chemical reactivity. The results of these studies are compiled in Scheme 17, which shows that both of these reactive species can be





SCHEME 18

trapped by alkynes to produce the stannacyclopropene **79** (91) and the 1,2-distannacyclobut-3-ene **80** (92). It has been proposed that the formation of this latter compound proceeds via 2 + 2 addition of the distannene **72** to phenylacetylene. However, the sequential addition of the stannylene monomer **78** to the alkyne, followed by insertion of another stannylene equivalent into the Sn–C bond of the intermediate stannacyclopropene, cannot be ruled out. Indeed, this latter mechanism was previously proposed to account for the formation of both the stannacyclopropene **81** (93) and the 1,2-distannacyclobut-3-ene **82** (94) from the stannylene **15** according to Scheme 17. Perhaps more compelling evidence for the direct addition to the distannene **72** is provided by Weidenbruch and co-workers (95,96), who utilized the cyclotristannane **12** once more to generate **72** in situ, which was then reacted with various chalcogens, as shown in Scheme 18. With sulfur, the 1,2-dithiadistannetane **83** was produced, along with its isomer **84** (95), whereas with selenium and tellurium, only the corresponding three-membered ring compounds **85** and **86**, respectively, were isolated (96).

## VI

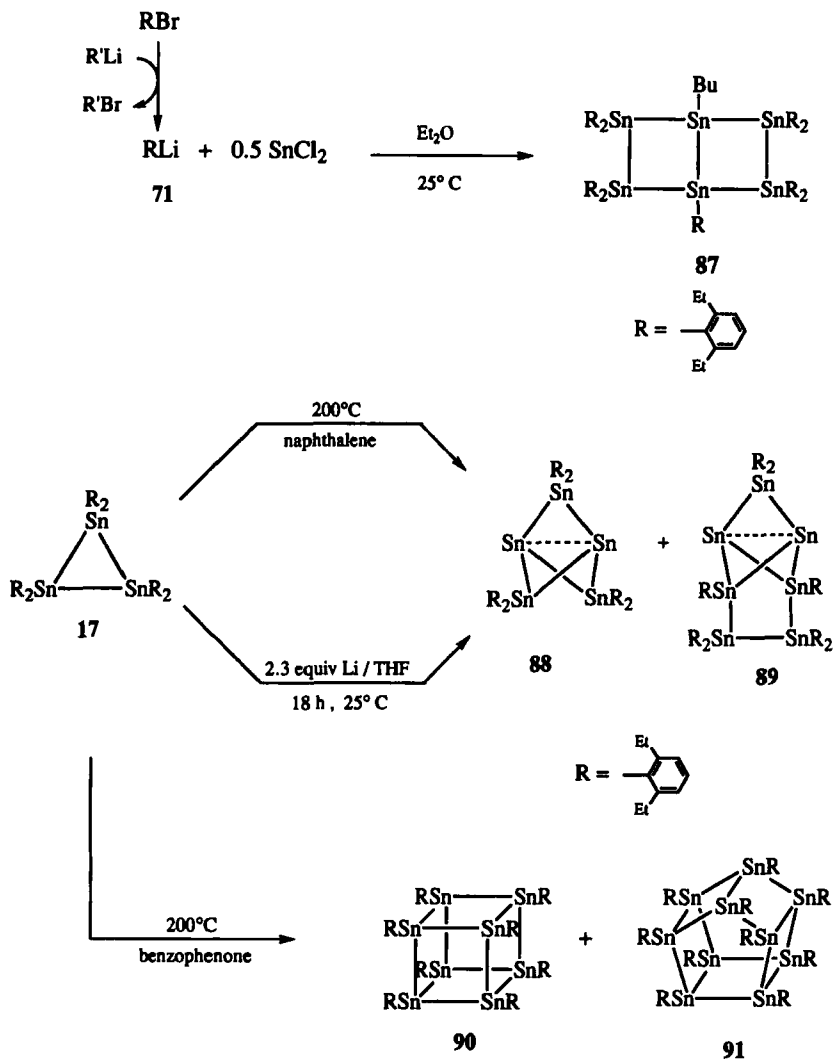
### Polycyclic Polystannanes

#### A. Synthesis

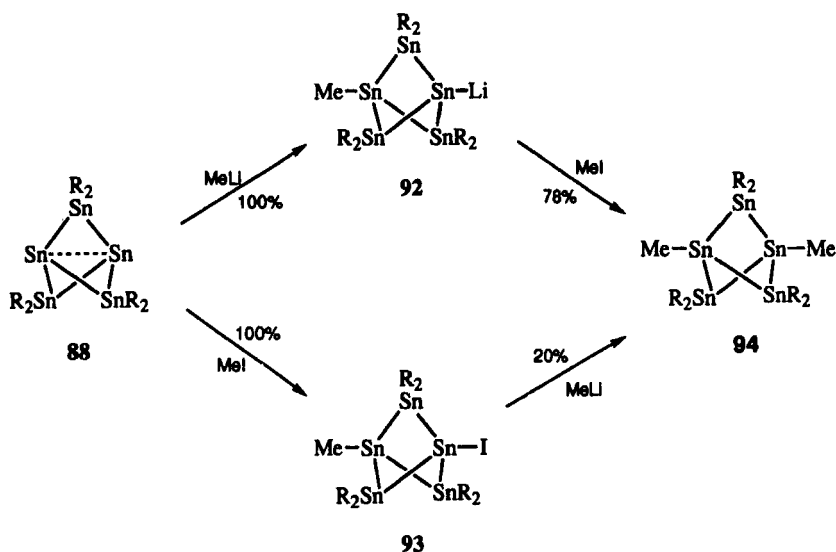
As late as 1988, there were no known examples of polycyclic polystannanes reported in the literature. However, through the careful fractionation of complex mixtures of products obtained from various oligomeriza-

tion reaction processes, a number of colored compounds were isolated, characterized, and found to be derivatives of a structurally diverse array of polycyclic polystannanes. These studies have been the subject of earlier reviews (97), and thus only the salient features will be presented here.

As shown in Scheme 19, the first example of a polycyclic polystannane, the bicyclo[2.2.0]hexastannane **87**, was obtained from fractionation of the



SCHEME 19

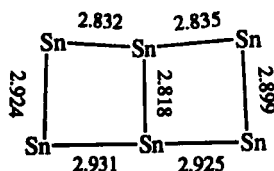


SCHEME 20

mixture of compounds obtained from the reaction of the aryllithium reagent **71** with tin dichloride in diethyl ether at 0°C (**83**). Interestingly, this compound was found to be stable towards air oxidation in both solution and in the solid state. A more surprising result, however, is the discovery that simple thermolysis of the cyclotristannane **17** at 200°C in various solvents, such as xylenes, naphthalene, and benzophenone, provides a mixture of compounds from which the perstanna[1.1.1]propellanes **88** and **89** and the perstanna-[*n*]-prismanes **90** (*n* = 4) and **91** (*n* = 5) can be isolated (**28,39,98,99**). Later it was discovered that the [1.1.1]propellanes **88** and **89** could also be obtained through reaction of the cyclotristannane **17** with lithium metal in tetrahydrofuran, as shown in Scheme 19 (**39**). Finally, it has been demonstrated that the pentastanna[1.1.1]propellane is a good precursor for the synthesis of the bicyclo[1.1.1]pentastannanes **92-94** via the reactions shown in Scheme 20 (**100,101**).

### B. Structural Studies

Given the unique frameworks associated with the polycyclic polystannanes shown in Scheme 19, it is fortunate that each of these compounds could be obtained in crystalline form and subjected to crystallographic analysis. It is also fortunate that, in each case, the parent compounds for these frameworks have been the subject of theoretical studies, and this



SCHEME 21

allows then for much-needed correlations between theory and experiment. Regarding the bicyclo[2.2.0]hexastannane **87**, crystallographic analysis provides a mean Sn–Sn bond length of 2.881 Å, which is within the expected range (83). However, inspection of the individual Sn–Sn bond lengths in this molecule reveal how relative differences in nonbonded interactions between the organic substituents can severely distort the  $\sigma$ -bonded framework away from its anticipated  $C_{2v}$  symmetric geometry, as shown in Scheme 21. Surprisingly, the bridgehead–bridgehead Sn–Sn bond in this compound is the shortest, at 2.818 Å, whereas calculations predict that it should be the longest, at 2.883 Å (102). In this case, it is likely that the nonbonded interactions in **87** enforce a “steric compression” of the central Sn–Sn bond rather than an elongation, which is their usual mode of action. Each of the four-membered rings in **87** are puckered rather than planar, and the mean of the Sn–Sn–Sn angles that define these rings is 89.9°. Of more important note is the average bond angle between the mean planes formed by these rings, which is 132.1° as opposed to the corresponding value of 113.6° that is calculated for the parent system. This structural discrepancy is once again most likely the result of the collaboration between strong nonbonded interactions and small-force constants for Sn–Sn–Sn bond angle deformations.

[1.1.1]Propellanes are a class of nonclassical structures, since they possess bridgehead atoms having formally inverted tetrahedral geometries that force the four bonds from each of the bridgehead atoms to lie within the same hemisphere. Given this configuration, theoretical investigations have long sought to determine the stability and reactivity of these molecular frameworks prior to the availability of representative synthetic derivatives. The isolation and structural characterization of the two perstanna[1.1.1]propellanes, **88** and **89**, thus represent a unique opportunity to test the accuracy of these predictions. The molecular structure of **88** is shown in Fig. 13; in the solid state, this compound is chiral, with  $D_3$  symmetry. Due to hindered rotation about the Sn–C bonds, the  $^1\text{H}$  NMR spectrum of **88** taken at 20°C show multiple resonances due to inequivalencies of the ethyl and phenyl protons, although at 100°C, partial rotations

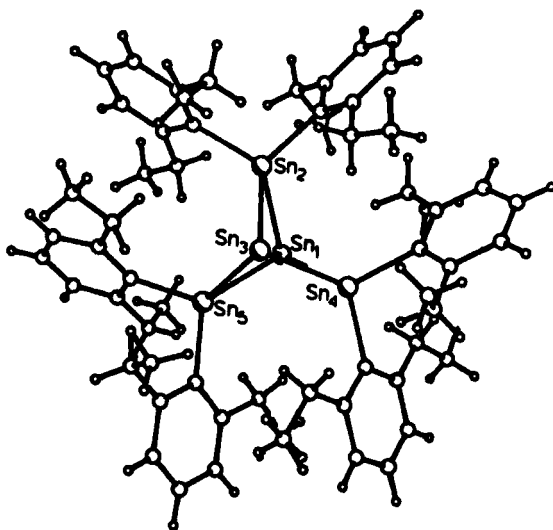


FIG. 13. Molecular structure of the pentastanna[1.1.1]propellane **88**. Reprinted with permission from Sita and Bickerstaff (28).

of the phenyl substituents serve to remove some but not all of these inequivalencies. (i.e., the  $D_3$  symmetry is preserved). The mean  $\text{Sn}_{\text{br}}\text{--}\text{Sn}_{\text{bh}}$  (br = bridging, bh = bridgehead) bond length in **88** is 2.858 Å, whereas from the crystal structure of **89**, the corresponding value is determined to be slightly contracted, at 2.845 Å. Most importantly, the  $\text{Sn}_{\text{bh}}\text{--}\text{Sn}_{\text{bh}}$  bond length in **88** is 3.367 Å, while once again this same value is slightly smaller for the heptastanna[1.1.1]propellane **89**, at 3.348 Å. Both of these values are much longer than even that of the distannane **16** (cf. 3.052 Å, Table I), and it is therefore natural to ask whether these former distances allow for true Sn–Sn bonding. In this regard, it is important to point out that the crystal structure reported for the bicyclo[1.1.1]pentastannane **93** reveals that the structural parameters for the tin-bonded framework of this compound are virtually identical to those of **88**, with a  $\text{Sn}_{\text{bh}}\text{--}\text{Sn}_{\text{bh}}$  nonbonded distance of 3.361 Å (100). Overall, then, the data tend to suggest that the bridgehead–bridgehead interaction in compounds **88** and **89** is either nonexistent or very weak at best. This view is supported by recent theoretical studies of the parent pentastanna[1.1.1] propellane compound, which provide a calculated  $\text{Sn}_{\text{bh}}\text{--}\text{Sn}_{\text{bh}}$  distance of between 3.463 and 3.495 Å and conclude that no “formal” bond connects these two atoms (87,103).

The crystal structures of the perstanna-[ $n$ ]-prismanes **90** and **91** are

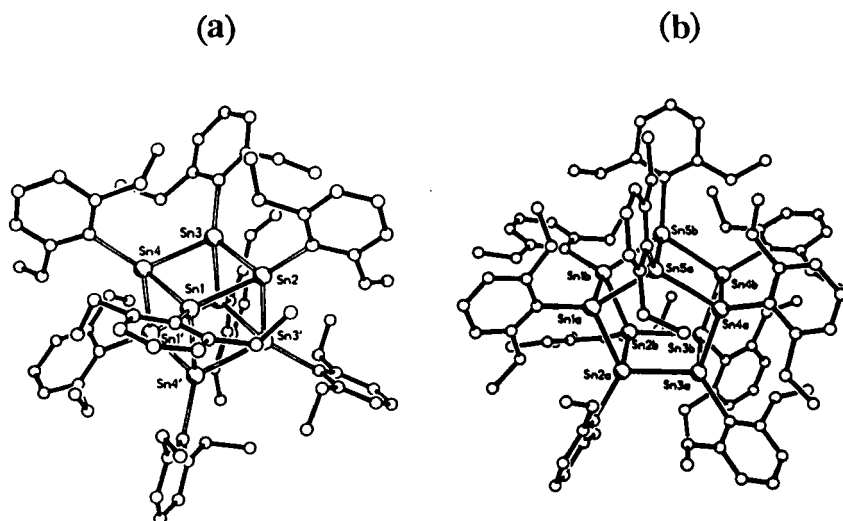


FIG. 14. Molecular structures of the perstanna- $[n]$ -prismanes: (a) compound **90**, and (b) compound **91**. Reprinted with permission from Sita and Kinoshita (98,99).

shown in Fig. 14. In compound **90** the mean Sn–Sn bond length is 2.854 Å, whereas for compound **91** the mean Sn–Sn bond length within, and between, the five-membered rings is 2.856 Å. All of the Sn–Sn–Sn bond angles in these two compounds are very close to those expected on the basis of geometric considerations, and this lends support to the view that steric interactions between the 2,6-diethylphenyl substituents are minimal and do not contribute to significant distortions of the polystannane frameworks. Interestingly, the mean Sn–Sn bond length determined for **90** is slightly smaller than that predicted for the parent system (104).

### C. Properties and Reactivity

All of the polycyclic polystannanes reported to date are thermally robust in solution to temperatures of at least 200°C. For the bicyclo[2.2.0]hexastannane derivative **87**, this is not too surprising, since the calculated strain-energy value for the parent compound is still ca. 12 kcal mol<sup>−1</sup> less than the parent cyclotristannane system (102). However, the parent perstanna- $[n]$ -prismanes for  $n = 4$  and 5 are expected to be more ring-strained than cyclotristannane (cf. 73.2 and 61.0 kcal mol<sup>−1</sup>, respectively) (99,104); therefore, the thermal stability of the two compounds, **90** and **91**, suggest that these compounds are kinetically stable by virtue of signifi-

cantly high barriers toward Sn–Sn bond dissociation. Although thermally robust, the bicyclo[1.1.1]pentastannane **94** has been shown to regenerate the pentastanna[1.1.1]propellane **88** upon photolysis, and the driving force for this process has been interpreted as arising from the release of strong steric interactions at the bridgehead positions (101).

All of the polycyclic polystannanes reported to date are visibly colored, and their electronic spectra accordingly exhibit low energy-absorption maxima. Perhaps the most striking examples are the perstanna[1.1.1]propellanes, **88** and **89**, solutions of which are blue-violet and burgundy in color, and which show corresponding absorption maxima at  $\lambda_{\max}$  558 ( $\epsilon_{\max}$  1540) and 528 nm (4541), respectively. A correlation between these absorption maxima and Sn<sub>br</sub>–Sn<sub>bh</sub> bond length has been used to suggest that a significant bridgehead–bridgehead bonding interaction in perstanna[1.1.1]propellanes does in fact exist. For the two perstanna-[*n*]-prismanes, **90** and **91**, the electronic spectra are quite different, with unique absorption maxima for **90** occurring at  $\lambda_{\max}$  275 nm ( $\epsilon_{\max}$  112,000) and 450 nm ( $\epsilon_{\max}$  2,000), while for **91** no distinct absorptions can be discerned [ $\lambda$  270 nm ( $\epsilon$  83,000), 350 nm ( $\epsilon$  6,100)]. The bicyclo[2.2.0]hexastannane **87** is also highly colored, with absorptions occurring at  $\lambda_{\max}$  307 nm ( $\epsilon_{\max}$  37,900) and 360 nm (13,690). Finally, the bicyclo[1.1.1]pentastannanes **93** and **94** display significantly different electronic spectra, with the former being red-colored and having an unusual absorption maxima at  $\lambda_{\max}$  500 nm ( $\epsilon_{\max}$  1700) that is absent in the latter.

Given the unique structures of the polycyclic polystannanes that have been isolated to date, these compounds provide an opportunity to explore the relationships between structure and  $^{119}\text{Sn}$  NMR parameters. For the [1.1.1]propellane **88**, the chemical shifts of Sn<sub>br</sub> and Sn<sub>bh</sub> occur at 356 and –1751 ppm, respectively. The values for the coupling constants,  $^1J(^{119}\text{Sn}_{\text{br}}-^{117}\text{Sn}_{\text{bh}})$  and  $^2J(^{119}\text{Sn}_{\text{br}}-^{117}\text{Sn}_{\text{br}})$  in this compound are 3975 and 262 Hz, respectively. Unfortunately  $^1J(^{119}\text{Sn}_{\text{bn}}-^{117}\text{Sn}_{\text{bh}})$  could not be observed for this compound. The values obtained above for **88** can be contrasted to those determined for the bicyclo[1.1.1]pentastannane **94** by  $^{119}\text{Sn}$  NMR spectroscopy. In this compound the chemical shifts for Sn<sub>br</sub> and Sn<sub>bh</sub> are now at –334 and –247, respectively (105), and the values for the coupling constants,  $^1J(^{119}\text{Sn}_{\text{br}}-^{117}\text{Sn}_{\text{bh}})$ ,  $^2J(^{119}\text{Sn}_{\text{br}}-^{117}\text{Sn}_{\text{br}})$ , and  $^2J(^{119}\text{Sn}_{\text{bh}}-^{117}\text{Sn}_{\text{bh}})$ , are 125, 1387, and 7390 Hz, respectively. These latter values are fairly unusual, and the large size for  $^2J(^{119}\text{Sn}_{\text{bh}}-^{117}\text{Sn}_{\text{bh}})$  suggests that additive contributions from multiple pathways within a polycyclic framework play an important role in determining the magnitude of coupling constants in polycyclic polystannanes. The value for the one-bond coupling constant,  $^1J(^{119}\text{Sn}_{\text{br}}-^{117}\text{Sn}_{\text{bh}})$ , is small but still within the range expected on the basis of a bond-length dependence for this parameter. What is surprising, however, is that this coupling constant is dramatically tem-

perature dependent, starting at a value of 200 Hz at 214 K and decreasing to a value of 38 Hz at 373 K. This behavior is quite unusual for a stereochemically rigid polyatomic molecule. It has been interpreted as arising from the increase in nonbonded steric interactions at elevated temperatures, which serve to facilitate a breathing-mode expansion of the bicyclo[1.1.1]pentastannane framework and thereby to shift the Sn–Sn bond lengths and Sn–Sn–Sn bond angles away from their equilibrium values. As a final note concerning the  $^{119}\text{Sn}$  NMR spectra of polycyclic polystannanes, the spectra for the perstanna-[*n*]-prismanes, **90** and **91**, reveal chemical shifts for these compounds of 44.3 and  $-21.3$  ppm, respectively. For compound **90**, the observed coupling constants,  $^1J(^{119}\text{Sn}-^{117}\text{Sn})$  and  $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ , have values of 1576 and 1345 Hz, respectively. In compound **91**, the coupling constants between tin atoms in different five-membered rings are  $^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 693$  Hz and  $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 1224$  Hz, whereas those between tin atoms in the same five-membered rings are  $^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 3312$  Hz and  $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 90$  Hz. It is interesting to note that in both **90** and **91**, the expected  $^3J(^{119}\text{Sn}-^{117}\text{Sn})$  coupling constants are not observed, presumably due to a Karplus correlation between dihedral angle and vicinal coupling constants that predicts that the magnitude of these particular coupling constants should be near zero due to the  $90^\circ$  dihedral angle in both molecular frameworks.

Regarding the chemical reactivity of polycyclic polystannanes, to date this subject has not been thoroughly investigated. However, it can be anticipated that this will be a rich field for study. In particular, these compounds should be interesting starting materials for the synthesis of new classes of compounds. Some demonstration of this was shown in Scheme 20 by the synthesis of bicyclo[1.1.1]pentastannanes from the pentastanna[1.1.1]propellane **88**. It has also been shown that both **88** and **89** can be chemically reduced to the corresponding dianions without cleaving any of the Sn–Sn bonds of their polycyclic frameworks. These dianions might then serve to generate other compounds through their reaction with various electrophiles. Finally, another class of reaction that should prove interesting is the insertion of chalcogen atoms into the tin-bonded frameworks of the perstanna-[*n*]-prismanes, **90** and **91**.

## VII

### CONCLUSION

From the review of our knowledge regarding polystannanes presented here, several points become obvious. First, a wide structural diversity for polystannanes does exist. Second, by virtue of the unique properties



associated with their Sn-Sn  $\sigma$ -bonded frameworks, polystannanes are an important class of compound to study. Finally, there remains several large gaps in our knowledge concerning the structure/property relationships of polystannanes. However, it remains the hope that as new synthetic methodologies are developed, most of these holes will be filled through the acquisition and investigation of new derivatives of several different structural classes.

## REFERENCES

- (1) Rundle, R. E. *J. Phys. Chem.* **1957**, 61 45.
- (2) Miller, J. R. *J. Chem. Soc.* **1961**, 4452; **1965**, 713.
- (3) Little, W. A. *Phys. Rev.* **1964**, 134, 1416.
- (4) Ferrell, R. A. *Phys. Rev. Lett.* **1964**, 13, 330.
- (5) Pitt, C. G.; Monteith, L. K.; Ballard, L. F.; Collman, J. P.; Morrow, J. C.; Roper, W. R.; Ulku, D. *J. Am. Chem. Soc.* **1966**, 88, 4286; Collman, J. P.; Hoyano, J. K.; Murphy, D. W. *ibid.* **1973**, 95, 3424; Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, 13, 1.
- (6) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, 10, 1647.
- (7) A novel solid-phase approach to the synthesis of catenated metal oligomers has been presented, however, to date, demonstration of its utility is confined to a single three-metal example, see Burlitch, J. M.; Winterton, R. C. *J. Am. Chem. Soc.* **1975**, 97, 5605.
- (8) Creemer, H. M. J. C.; Verbeek, F.; Noltes, J. G. *J. Organomet. Chem.* **1968**, 15, 125.
- (9) For some recent reviews, see (a) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Agnew. Chem., Int. Ed. Engl.* **1991**, 30, 902; (b) Sekiguchi, A.; Sakurai, H. In "The Chemistry of Inorganic Ring Systems"; Steudel, R., Ed., Elsevier: New York, 1992, pp. 101-125.
- (10) Miller, R. D.; Michl, J. *J. Chem. Rev.* **1989**, 89, 1359; Zeigler, J. M.; Fearson, R. W. G. *Adv. Chem. Ser.* **1990**, 224.
- (11) Bigelow, R. W. *Chem. Phys. Lett.* **1986**, 126, 63; Balaji, V.; Michl, J. *Polyhedron* **1991**, 10, 1265; Ortiz, J. V. *ibid.*, 1285.
- (12) For a previous review, see: Adams, S.; Dräger, M. *Main Group Metal Chemistry* **1988**, XI, 151.
- (13) Jolly, W. L. *Angew. Chem.* **1960**, 72, 268; *J. Chem. Soc.* **1961**, 83, 335.
- (14) Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: New York, 1970; Davies, A. G.; Smith, P. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: New York, 1982, pp. 519-627 in Vol. 2.
- (15) Neumann, W. P.; Schneider, B.; Sommer, R. *Justus Liebigs Ann. Chem.* **1966**, 692, 1-11.
- (16) Gielen, M.; Tondeur, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 81.
- (17) Kandil, S. A.; Allred, A. L. *Chem. Soc. A* **1970**, 2987.
- (18) Weidenbruch, M.; Schlaefke, J.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1991**, 414, 319.
- (19) Neumann, W. P.; Pedain, J. *Tetrahedron Lett.* **1964**, 2461.
- (20) Mathiasch, B. *Inorg. Nucl. Chem. Lett* **1977**, 13, 13; Mathiasch, B. *Synth. React. Inorg. Met-Org. Chem.* **1977**, 7, 227.
- (21) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, 107, 6390.
- (22) Brown, P.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1992**, 435, 265.
- (23) Sita, L. R. Ph. D. Dissertation, MIT, Cambridge, MA, 1985.

- (24) Puff, H.; Breuer, B.; Gehrke-Brinkmann, G.; Kind, P.; Reuter, H.; Schuh, W.; Wald, W.; Weidenbrüch, G. *J. Organomet. Chem.* **1989**, *363*, 265.
- (25) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.
- (26) Al-Allaf, T. A. K.; Eaborn, C.; Hitchcock, P. B.; Lappert, M. F.; Pidcock, A. J. *Chem. Soc., Chem. Commun.* **1985**, 548.
- (27) Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630.
- (28) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454.
- (29) Sanz, J. F.; Marquez, A. J. *Phys. Chem.* **1989**, *93*, 7328.
- (30) Preut, H.; Haupt, H.-J.; Huber, F. Z. *Anorg. Allg. Chem.* **1973**, *396*, 81.
- (31) Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. J. *Am. Chem. Soc.* **1977**, *99*, 1916.
- (32) Schleyer, P. v. R.; Kaupp, M.; Hampel, F.; Bremer, M.; Mislow, K. *J. Am. Chem. Soc.* **1992**, *114*, 6791.
- (33a) Tagliavani, G.; Faleschini, S.; Pilloni, G.; Plazzogna, G. *J. Organomet. Chem.* **1966**, *5*, 136 (synthesis).
- (33b) Schneider, C.; Dräger, M. *J. Organomet. Chem.* **1991**, *415*, 349–362 (X-ray).
- (34) Morris, H.; Byerly, W.; Selwood, P. W. *J. Am. Chem. Soc.* **1942**, *64*, 1727 (synthesis); Gilman, H.; Rosenberg, S. D. *J. Org. Chem.* **1953**, *18*, 1554 (synthesis); Schneider-Koglin, C.; Behrends, K.; Dräger, M. *J. Organomet. Chem.* **1993**, *448*, 29 (X-ray).
- (35) Ref. 28; see supplementary material.
- (36) Adams, S.; Dräger, M.; Mathiasch, B. Z. *Anorg. Allg. Chem.* **1986**, *532*, 81 (X-ray).
- (37) Drenth, W.; Janssen, M. J.; Van Der Kerk, G. J. M.; Vliegenthart, J. A. *J. Organomet. Chem.* **1964**, *2*, 265.
- (38) Hauge, D. N.; Prince, R. H. *J. Chem. Soc.* **1965**, 4690.
- (39) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1992**, *114*, 7024.
- (40) Gager, H. M.; Lewis, J.; Ware, M. J. *J. Chem. Soc., Chem. Commun.* **1966**, 616.
- (41a) Buschhaus, H.-U.; Neumann, W. P.; Apoussidis, T. *Liebigs Ann. Chem.* **1981**, 1190.
- (41b) El-Faragy, A. F.; Lehnig, M.; Neumann, W. P. *Chem. Ber.* **1982**, *115*, 2783.
- (42a) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.
- (42b) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.
- (43a) Mitchell, T. N. *J. Organomet. Chem.* **1974**, *70*, C1.
- (43b) Mitchell, T. N.; Walter, G. J. *Chem. Soc., Perkin Trans. 2*, **1977**, 1842.
- (44a) Kennedy, J. D.; McFarlane, W. J. *Chem. Soc., Chem. Commun.* **1974**, 983.
- (44b) Kennedy, J. D.; McFarlane, W.; Pyne, G. S.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **1975**, 386.
- (44c) Kennedy, J. D.; McFarlane, W. J. *Chem. Soc., Dalton Trans.* **1976**, 1219–1223.
- (44d) Biffar, W.; Ebeling-Gasparis, T.; Noth, H.; Storch, W.; Wrackmeyer, B. *J. Magn. Reson.* **1981**, *44*, 54.
- (45) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.
- (46) Pereyre, M. "Tin in Organic Synthesis"; Butterworth: Boston, 1987.
- (47) See Table 1 in Ref. 41a.
- (48) Grugel, C.; Neumann, W. P.; Seifert, P. *Tetrahedron Lett.* **1977**, 2205.
- (49) Sommer, R.; Schneider, B.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1966**, *692*, 12.
- (50) Jousseau, B.; Chanson, E.; Bevilacqua, M.; Saux, A.; Pereyre, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1985**, *294*, C41.
- (51) Creemers, H. M. J. C.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 382; Creemers, H. M. J. C.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *7*, 237.
- (52) Sita, L. R. *Organometallics* **1992**, *11*, 1442.
- (53) Puff, H.; Bach, C.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1986**, *312*, 313.
- (54) Adams, S.; Dräger, M. *Agnew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255.

- (55) Farrar, W. V.; Skinner, H. A. *J. Organomet. Chem.* **1964**, *1*, 434.
- (56) Adams, S.; Dräger, M. *J. Organomet. Chem.* **1985**, *288*, 295.
- (57) Gilman, H.; Artwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369; Sakurai, H.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1894.
- (58) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471.
- (59) Drenth, W.; Noltes, J. G.; Bulten, E. J.; Creemers, H. M. J. C. *J. Organomet. Chem.* **1969**, *17*, 173.
- (60) Takeda, K.; Shiraishi, K. *Chem. Phys. Lett.* **1992**, *195*, 121.
- (61) Puff, H.; Bongartz, A.; Sievers, R.; Zimmer, R. *Agnew. Chem., Int. Ed. Engl.* **1978**, *17*, 939.
- (62) Grugel, C.; Lehnig, M.; Neumann, W. P.; Sauer, J. *Tetrahedron Lett.* **1980**, 273.
- (63) Puff, H.; Bongartz, A.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1983**, *248*, 61.
- (64) Willemsens, L. C.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1964**, *2*, 260.
- (65) Mitchell, T. N.; El-Behairy, M. *J. Organomet. Chem.* **1977**, *141*, 43.
- (66) Kobayashi, K.; Kawanisi, M.; Hitomi, T.; Kozima, S. *J. Organomet. Chem.* **1982**, *233*, 299–311.
- (67) Klaui, W.; Werner, H. *J. Organomet. Chem.* **1973**, *54*, 331.
- (68) For early work related to the synthesis of monomeric stannylene species, see (a) Krause, E.; Becker, R. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 173; (b) Krause, E.; Pohland, R.; *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 532; (c) Baker, G.; Gelius, R. *Chem. Ber.* **1958**, *91*, 829; (d) Jensen, K. A.; Clauson-Kaas, N. Z. *Anorg. Allg. Chem.* **1943**, *250*, 277; (e) Kuivila, H. G.; Beumel, O. F., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 3250.
- (69) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387, and references cited therein.
- (70) Zilm, K.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.
- (71) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785.
- (72) Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; von Schnering, H. G.; Marsman, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1846.
- (73) Neumann, W. P.; König, K. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 212; Neumann, W. P.; König, K. *Justus Liebigs Ann. Chem.* **1964**, 677, 1.
- (74) Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310.
- (75) Neumann, W. P.; König, K. *Justus Liebigs Ann. Chem.* **1964**, 677, 12; Neumann, W. P.; Pedain, J. *ibid.* **1962**, *672*, 34; Neumann, W. P.; Pedain, J.; Sommer, R. *ibid.* **1966**, *694*, 9; Neumann, W. P.; König, K. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 751.
- (76) Puff, H.; Bach, C.; Reuter, H.; Schuh, W. *J. Organomet. Chem.* **1984**, *277*, 17.
- (77) Dräger, M.; Mathiasch, B.; Ross, L.; Ross, M. Z. *Anorg. Allg. Chem.* **1983**, *506*, 99.
- (78) Jousseau, B.; Noriet, N.; Pereyre, M.; Saux, A.; Francès, J.-M. *Organometallics* **1994**, *13*, 1034.
- (79) Belsky, V. K.; Zemlyansky, N. N.; Kolosova, N. D.; Borisova, I. V. *J. Organomet. Chem.* **1981**, *215*, 41.
- (80) Watta, B.; Neumann, W. P.; Sauer, J. *Organometallics* **1985**, *4*, 1954.
- (81) Lappert, M. F.; Leung, W. P.; Raston, C. L.; Thorne, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1982**, *233*, C28.
- (82) Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Devereaux, M. M.; Kelly, N. B. *J. Organomet. Chem.* **1991**, *414*, C9.
- (83) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 3769.
- (84) Brady, F. J.; Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Devereux, M. M.; Lawless, G. A. *J. Organomet. Chem.* **1991**, *241*, 199.

- (85) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834.
- (86) Neumann, W. P.; Fu, J. J. *Organomet. Chem.* **1984**, *273*, 295–302; Fu, J.; Neumann, W. P. *ibid.*, *272*, C5–C9.
- (87) Nagase, S. *Polyhedron* **1991**, *10*, 1299.
- (88) For another theoretical study of cyclotristannane and cyclotetrastannane, see Rubio, J.; Illas, F. J. *Mol. Struct. (Theochem.)* **1984**, *110*, 131.
- (89) Puff, H.; Gattermayer, R.; Hundt, R.; Zimmer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 547.
- (90) Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Devereux, M. M. *J. Organomet. Chem.* **1991**, *411*, C3.
- (91) Sita, L. R.; Bickerstaff, R. D. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 31.
- (92) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1992**, *125*, 563.
- (93) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208.
- (94) Sita, L. R.; Kinoshita, I.; Lee, S. P. *Organometallics* **1990**, *9*, 1644.
- (95) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 962.
- (96) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834.
- (97) Sita, L. R.; Kinoshita, I. In "Inorganic and Organometallic Oligomers and Polymers"; Harrod, J. F.; Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; Sita, L. R. *Acc. Chem. Res.* **1994**, *27*, 191.
- (98) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865.
- (99) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856.
- (100) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839.
- (101) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 5070.
- (102) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1990**, 630.
- (103) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247.
- (104) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.
- (105) Ref. 101, see supplementary material.

This Page Intentionally Left Blank

# Index

## A

- Acyltris(trimethylsilyl)silane, 21–22
- Adamantanone, 40
- Adsorption, alkyl halides on metal surface, 63–65, 73
- Alcohols, synthesis, alkane oxidation, 169
- Aldehydes, reduction with TPPMS complexes, 174–175
- Alkanes, reactions, 167–170
- Alkenes, reactions, 171–172, 174
- $\beta$ -Alkoxysilanes, 40
- (Alkoxysilyl)lithium, 19–20
- Alkyl bromides, metal corrosion in seawater, 71–74
- Alkylchromium(III) complexes, in aqueous solution, 156–160
- Alkyl–cobalt complexes, 108
- Alkylcobalt(III) complexes, in aqueous solution, 160–162
- Alkyl–gold complexes, 108
- Alkyl groups, adsorbed on metal surface, 64–65
- Alkyl halides
  - adsorption on metal surfaces, 63–65, 73
  - alkylchromium(III) complex synthesis from, 156–157
  - alkylcobalt(III) complex synthesis from, 160–161
  - hydrolysis, 71
  - metal leaching and corrosion, 71–74
  - nonsynthetic applications, 69–74
  - physical properties, 61
  - reactions with metal, 59, 61–63, 65–69
    - addition of water, 70–71
    - Direct Process Reaction, 60, 67–68, 69, 74–75
    - Grignard reaction, 66–67
- Alkyl iodides, 63, 71–74
- Alkyl–iron complexes, 108, 110
- Alkyl–manganese complexes, 108, 110
- Alkyl–metal compounds
  - in aqueous solution, 155–156
  - alkylchromium(III) complexes, 156–160
  - alkylcobalt(III) complexes, 160–162
  - alkylplatinum(III) complexes, 162–163
  - metal carbonyl complexes, 163–164
  - M–C bond distances, 105–112
- Alkyl–molybdenum complexes, 108
- Alkyl–palladium complexes, 108
- Alkylphosphines, 165–166
- Alkyl–platinum complexes, 108
- Alkylplatinum(III) complexes, in aqueous solution, 162–163
- Alkyl–ruthenium complexes, 108
- Alkylsilyl anions, 11–16, 50
- Alkyl–tungsten complexes, 108
- Alkyl–zirconium complexes, 108, 109
- Alkynes, organic, 102, 133–134
- Alkynyl bond, 80
- Alkynyl–cobalt complexes, 108, 111
- Alkynyl–gold complexes, 89, 108, 111–113, 119
- Alkynyl–iron complexes, 83–84, 89, 99, 104, 108, 110, 115, 119–120
- Alkynyl ligand, structural *trans* influences, 117–120
- Alkynyl–manganese complexes, 108, 110, 114–115
- Alkynyl–metal complexes, 79, 139–140
  - bonding, 80–82
    - electron spectroscopy, 84–88
    - molecular-orbital calculations, 83–84
    - Mössbauer spectroscopy, 89
    - NMR spectroscopy, 81, 89
    - photoelectron spectroscopy, 83–84
    - vibrational spectroscopy, 120–139
    - X-ray crystallography, 90–120
  - luminescence, 88
  - terminal complexes, 90–99, 103

Alkynyl-metal redox congeners, M-C bond distances, 115-116  
 Alkynyl-molybdenum complexes, 85, 100, 108, 115  
 Alkynyl-nickel complexes, 87, 89  
 Alkynyl-palladium complexes, 87, 89, 108, 111  
 Alkynyl-phosphorane ligands, 114  
 Alkynyl-platinum complexes, 87-89, 108, 111, 113, 117-118, 139  
 Alkynyl-ruthenium complexes, 104-105, 108, 110-111, 114, 117  
 Alkynyl-silicon complexes, 101-102, 104, 116-117  
 Alkynyl-titanium complexes, 84  
 Alkynyl-tungsten complexes, 85, 89, 108, 110, 112, 113  
 Alkynyl-vanadium complexes, 89, 112, 113  
 Alkynyl-zirconium complexes, 108, 109  
 Allylic chlorides, carbonylation, 175  
 Allylsilanolate anion, 20  
 (Allyl)silylcuprate, 43  
 (Amino)alkylchlorosilanes, 19  
 [(Amino)phenylsilyl]lithium, 17-18  
 Aminosilyl anions, 42  
 (Aminosilyl)lithium, 18, 42  
 (Aminosilyl)magnesium, 19  
 Antimony, reaction with alkyl halides, 72  
 Arenes, hydrogen-deuterium exchange, 167  
 Arylsilyl anions, 3-11, 50  
 Asymmetric catalysis, chiral sulfonated phosphines, 179-181

## B

Benzosilole anions, 25  
 Benzyl bromide, reaction with metals, 73  
 Bicyclo[2.2.0]hexastannanes, 233-234, 235, 237, 238  
 Bicyclo[1.1.1]pentastannanes, 234, 236, 238, 239  
 Biological methylation, 71  
 Bis[bis(trimethylsilyl)methyl]tin, 194  
 Bis(cyclopentasilanyl)mercury, 33  
 Bis-silyl derivatives, Group 12 metals, 3  
 1,2-Bis(2,4,6-triisopropylphenyl)-1,1,2,2-tetra(*r*-butyl)distannane, 199

Bis(trimethylsilyl)magnesium, 13  
 Bonding  
   alkynyl bond, 80  
   carbon-carbon triple bond, 80, 100-105, 121-138, 172  
   carbon-halogen bond scission, 60, 63-64  
   carbon-metal bond, 105-116, 136-137  
   carbon-ruthenium bond, 88-89, 104, 114  
   C-R bond, 116-117, 136-137  
   gold-phosphorus bond, 119  
   platinum-chlorine bond, 117-118, 119  
   tin-tin bond, 203-204, 209-210, 222-223, 235  
 Borosilyl anion, 46  
 Branched polystannanes, 215-217  
 Brass, leaching by alkyl halides, 73, 74  
 $\omega$ -Bromo-1-alkenes, 73  
 Bromocyclooctastannane, 225  
 2-Bromoethyl-diethyl phosphonate, 164-165  
 7-Bromoheptanenitrile, reaction with copper, 74  
 Bronze, leaching by alkyl halides, 74

## C

Cacodylic acids, 72  
 Carbon-carbon double bond, reduction, 172  
 Carbon-carbon triple bond, 80  
   bond distances, 100-105  
   reduction, 172  
   stretching frequencies, 121-138  
 Carbon-halogen bond  
   bond energy, 62  
   dipole moment, 60  
   scission, 63-64  
 Carbon-metal bond, 105-116, 136-137  
 Carbon monoxide-metal complexes, 114  
 Carbon-ruthenium bond, 88-89, 104, 114  
 Carbonylation, allylic chlorides, 175  
 Catalysis, homogeneous, *see* Homogeneous catalysis  
 Chiral phosphines, 179-181  
 Chlorine-platinum bond, 117-118, 119  
 1-Chloro-2-[*p*-(dimethylamino)phenyl]tetramethyldisilane, reaction with lithium, 36

Chlorodisilane, reactions, 11, 35–36  
 2-Chloroethyldimethylamine, 164  
 Chloromethane, formation, 167  
 1-Chloro-2-phenyltetramethyldisilane, reaction with lithium, 35–36  
 Chlorosilane, 2–4, 10–11, 26  
 Chromium, alkylchromium(III) complex, 156–160  
 Chromium–phenylethynyl complexes, 122, 135, 136  
 Cobalt, alkylcobalt(III) complexes, 160–162  
 Cobalt–alkyl complexes, 108  
 Cobalt–alkynyl complexes, 108, 111  
 Cobalt(II) cyanide complexes, as alkene hydrogenation catalysts, 171–172  
 Cobalt–phenylethynyl complexes, 125–126, 137  
 Copper  
   alkyl halide adsorption on, 64  
   corrosion in seawater, 71–74  
   reaction with alkyl halides, 73, 74  
 Copper(II) catalysts, 171  
 Corrosion, in seawater, alkyl halides and, 71–74  
 C–R bond, 116–117, 136–137  
 Crystallography, alkynyl–metal complexes, 90–120  
 Cyanoethynyl ligand, 111  
 Cyano–metal complexes, 81, 112–114  
 Cyclic voltammetry, metal–alkynyl complexes, 89–90  
 Cyclodextrins, 181–182  
 Cyclohexanes, catalytic reactions with platinum catalysts, 167–170  
 Cyclohexasilane, 33, 36  
 Cyclohexasilanyllithium, 32  
 Cyclohexastannanes, 221, 228  
 Cyclopentasilanes, ring-opening polymerization, 37–38  
 Cyclopentasilanyllithium, 33  
 Cyclopolystannanes, 217–232  
 Cyclotetrasilanes, ring-opening polymerization, 37  
 Cyclotetrastannanes, 207, 218, 221–226, 228, 230, 231  
 Cyclotristannanes, 222, 223, 226, 228, 230–232, 234  
 Cyclotristannoxanes, 230

## D

Decabutyltetrastannane, 205  
 Decamethylcyclopentasilane, 33  
 Decaphenylcyclopentasilane, 32  
 (Dialkoxysilyl)lithium, 20  
 Dialkylchalconides, 72  
 Dialkyltin dihalides, preparation, 69  
 Dialkylzinc compounds, 59  
 Diarylstannylene, 218, 231  
 1,2-Dibromo-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane, 193, 199  
 Dibutylcyanocuprates, 43  
 Dichlorodisilane, action of lithium on, 27  
 1,2-Dichlorodistannanes, 193  
 Dichlorosilanes, reductive coupling of, 34–35  
 1,2-Dichloro-1,1,2,2-tetrakis[bis(trimethylsilyl)methyl]distannane, 194, 199  
 1,2-Dichloro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane, 193  
 1,2-Dichloro-1,1,2,2-tetramethyldistannane, 199, 204  
 Dienes, hydrogenation to monoenes, 171–172  
 Diethyl maleate, formation, 182  
 Diethyl oxaloacetate, formation, 182  
 Dihalodisilane, 21  
 1,2-Dihalo-1,1,2,2,3,3,4,4-octa(*r*-butyl)tetrastannanes, 207  
 $\beta$ -Dihydrosilylation, 44  
 1,2-Diiodo-1,1,2,2-tetra(*r*-butyl)distannane, 207  
 Diisobutylaluminum hydride, 205–206  
 1,4-Dilithiooctaphenyltetrasilane, 32  
*gem*-Dilithiooligosilane, 31  
 1,5-Dilithiopentasilane, 32  
 1,1-Dilithio-silacyclopentadienes, 25  
 Dimetallapolyne complexes, 85, 109  
 $\alpha,\omega$ -Dimethoxypermethylopolysilanes, 37  
 (Dimethylamino)trimethylstannane, 215, 216  
 5,5-Dimethyldibenzosilole, 25  
 1,2-Dimethyl-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)distannane, 194  
 1,2-Dimethyltetrakis(2,4,6-triisopropylphenyl)distannane, 199



Diorganotin bisamides, 205, 221  
Diorganotin dichloride, 193  
Diorganotin dihydrides, 205, 221  
 $\alpha,\omega$ -Diphenylpermethylpolysilane, 35  
Diphenylphosphide, 164  
(2-Diphenylphosphinoethyl)trimethylammonium cation, 179  
1,2-Diphenyltetramethyldisilane, 37  
Diphenyltin, 218  
Direct Process Reaction, 60, 67–68, 69, 74–75  
1,2-Disilacylcobutane, 40  
Disilanes, 2–4, 10–12, 18  
Disilanyl anions, 26–28, 51–52  
Disilanylene 1,2-dianion, 27  
Disilanyllithium, 11, 26, 27, 40  
Disilanylpotassium, 26  
Disilenes, masked, 38–39  
1,1-Disodio-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 24  
1,2-Distannacyclobut-3-ene, 232  
Distannanes, 190–191, 210  
    mixed derivatives, 198–199  
    peralkyl derivatives, 195, 197–198  
    peraryl derivatives, 194–197, 200  
    properties, 199–203  
    reactivity, 203–204  
    structure, 194–199  
    synthesis, 191–194  
Distannene, 232  
1,2-Dithiadistannetane, 232  
Dodecabenzylicyclohexastannane, 221, 223  
Dodecamethylcyclohexasilane, 26, 32, 34–36  
Dodecamethylcyclohexastannane, 221, 228  
Dodecaphenylcyclohexastannane, 218, 222

## E

Electrochemical potentials, metal-alkynyl complexes, 89–90  
Electronic spectroscopy  
    alkynyl-metal complexes, 84–88  
    polystannanes, 199–202, 210–212  
Environmental hazards, methylmetal derivatives, 71  
Ethane, oxidation to alcohol, 169–170  
Ethers, oxidation of, 170  
Ethylbenzene, oxidation to alcohol, 169  
Ethyne ligands, 100, 101, 139

Extended-Hückel calculations, iron-alkynyl complexes, 83

## F

Fenske–Hall method, iron-alkynyl complexes, 83  
Fluorides, organic, 60  
(Fluorosilyl)lithium, 21, 47  
Formaldehyde, reaction with phosphine, 165

## G

Gold-alkyl complexes, 108  
Gold-alkynyl complexes, 89, 108, 111–113, 119  
Gold-phenylethynyl complexes, 131  
Gold-phosphorus bond, 119  
Grignard reactions, 66–67  
Grignard reagent, 59

## H

Hafnium-phenylethynyl complexes, 122, 135, 136  
 $\alpha$ -Halosilyl anions, 21  
Heptastanna[1.1.1]propellanes, 236  
Hexabenzyldistannane, 198, 200  
Hexa(*n*-butyl)distannane, 198  
Hexakis(2,6-diethylphenyl)cyclotristannane, 194  
Hexakis(2,6-diethylphenyl)distannane, 194, 197  
Hexakis(2-methylphenyl)distannane, 203  
Hexakis(2,4,6-triisopropylphenyl)cyclotristannane, 194  
Hexakis(trimethylsilyl)disilane, 28–29  
Hexamethyldistannane, 200  
Hexa(2-methylphenyl)distannane, 196–197  
Hexa(4-methylphenyl)distannane, 196  
Hexaphenyldisilane, cleavage reaction, 4  
Hexaphenyldistannane, 196, 199–200, 203  
Hexastannanes, 208–210, 211  
Hexa(*o*-tolyl)disilane, 4  
Homogeneous catalysis  
    asymmetric catalysis, 179–181  
    chiral sulfonated phosphines, 179–181  
    cobalt-cyanide complexes, 171–172  
    supramolecular-medium effects, 181–182

tertiary phosphine complexes, 172–174  
  TPPMS complexes, 174–175  
  TPPTS complexes, 175–178  
  TPTS complexes, 178–179  
transition-metal halides, 167–171  
Homolytic cleavage, metal–carbon bond, 158  
Hydroformylation  
  propene, 175–176  
  tertiary phosphine complexes as catalysts, 173–178  
Hydrogenation  
  alkenes, 171–172  
  propionaldehyde, 178  
  tertiary phosphine complexes as catalysts, 173–175, 178–179  
Hydrogen–deuterium exchange, 167  
Hydrosilane, enantiomeric, 6  
Hydrosilyl anions, 17  
Hydrostannolysis reaction, 191, 205, 215, 221

## I

Iodomethyl diplatinum(III) complex, 162–163  
Iridium, alkyl halide complex, 62  
Iridium–phenylethynyl complexes, 127–128, 132, 137, 138  
Iridium–TPPMS complex, 175  
Iron, reaction with alkyl halides, 73  
Iron–alkyl complexes, 108, 110  
Iron–alkynyl complexes, 83–84, 89, 99, 104, 108, 110, 115, 119–120  
Iron–phenylethynyl complexes, 123–124, 134–136

## K

Kinetic stabilization, 204

## L

Leaching, metals by alkyl bromides, 71–74  
Lead–sodium alloy, in preparation of tetraethyllead, 68–69  
Linear polystannanes  
  properties, 210–214  
  reactivity, 214–215

  structure, 208–210  
  synthesis, 205–208  
1-Lithio-1-*t*-butyl-2,3,4,5-tetraphenylsila-cyclopentadiene, 23  
1-Lithio-2,6-diethylbenzene, 221  
5-Lithio-5-methyldibenzosilole, 25  
1-Lithio-1-methyl-2,3,4,5-tetraphenylsila-cyclopentadiene, 24  
Lithium, reactions  
  with 1-chloro-2-[*p*-(dimethylamino)phenyl]tetramethyldisilane, 36  
  with chlorodisilane, 35–36  
  with 1-chloro-2-phenyltetramethyldisilane, 35–36  
  with dichlorodisilane, 27  
  disilane cleavage with, 2–4  
  with dodecamethylcyclohexasilane, 26, 32, 34–36  
Lithium diphenylphosphide, 164  
Lithium–phenylethynyl complexes, 122  
Lithium sila-enolate, 22  
Lithium tetrakis(trimethylsilyl)aluminate, 13  
Luminescence, metal–alkynyl complexes, 88

## M

Magnesium–alkyl halide reaction, 66–67  
Manganese–alkyl complexes, 108, 110  
Manganese–alkynyl complexes, 108, 110, 114–115  
Manganese–phenylethynyl complexes, 123, 136  
Masked disilenes, anionic polymerization, 38–39  
Metal–alkyl compounds, M–C bond distances, 105–112  
Metal–alkyl halide complexes, 62  
Metal alkyls  
  in aqueous solution, 155–156  
  alkylchromium(III) complexes, 156–160  
  alkylcobalt(III) complexes, 160–162  
  alkylplatinum(III) complexes, 162–163  
  metal–carbonyl complexes, 163–164  
  M–C bond distances, 105–112  
Metal–alkynyl complexes, 79, 139–140  
  bonding, 80–82  
  electronic spectroscopy, 84–88

- molecular-orbital calculations, 83–84
  - Mössbauer spectroscopy, 89
  - NMR spectroscopy, 81, 89
  - photoelectron spectroscopy, 83–84
  - vibrational spectroscopy, 120–139
  - X-ray crystallography, 90–120
  - luminescence, 88
  - terminal complexes, 90–99, 103
  - Metal–alkynyl redox congeners, M–C
    - bond distances, 115–116
  - Metal–carbon bond, 105–116, 136–137
    - homolytic cleavage, 158
  - Metal–carbon monoxide complexes, 114
  - Metal–carbonyl complexes, in aqueous solution, 163–164
  - Metal–cyano complexes, 81, 112–114
  - Metallabutadiyne complexes, 87, 109–110
  - Metal–phenylethylene complexes, 122–138
  - Metals
    - corrosion in seawater, alkyl halides and, 71–74
    - reactions with alkyl halides, 59, 61–63, 65–69
      - addition of water, 70–71
      - Direct Process Reaction, 67–68, 69, 74–75
      - Grignard reaction, 66–67
      - surface adsorption of alkyl halides, 63–65, 73
  - Methane, oxidation to methanol, 170
  - (Methoxysilyl)sodium, 20
  - Methylarsonic acid, 72
  - [(2-Methyl-2-butenyl)diphenylsilyl]cuprate, 43
  - Methylchlorosilanes, Direct Process Reaction, 67–68, 69, 74–75
  - Methylcobalamin, 155
  - Methylmercuric derivatives, 71
  - Methylmetal derivatives, environmental hazards, 71
  - Methylnickel(IV) compounds, 63
  - Methylsilicon(II) chloride, 68
  - Molecular-orbital calculations, alkynyl–metal complexes, 83–84
  - Molybdenum, reaction with benzyl bromide, 73
  - Molybdenum–alkyl complexes, 108
  - Molybdenum–alkynyl complexes, 85, 100, 108, 115
  - Molybdenum–phenylethynyl complexes, 122, 135, 136
  - Monoenes, diene hydrogenation to form, 171–172
  - Monosulfonated triphenylphosphine, *see* TPPMS
  - Mössbauer spectroscopy, alkynyl–metal complexes, 89
- N**
- Naphthalene, reduction reaction, 14
  - Nickel
    - alkyl halide adsorption on, 63–64
    - reaction with benzyl bromide, 73
  - Nickel–alkynyl complexes, 87, 89
  - Nickel–phenylethynyl complexes, 128, 135, 137
  - NMR spectroscopy
    - alkynyl–metal complexes, 81, 89
    - polystannanes, 202–203, 212–214, 216–217, 227–228, 238
    - silyl anions, 7–9, 26–27, 48–49
  - Nonamethylcyclopentasilanyl–potassium, 33
  - Nonaphenyltetrasilanyl–lithium, 32
  - Nonasilane, 32
- O**
- Octabutyltristannane, 205
  - Octa(*t*-butyl)tristannane, 207
  - Octaphenylcyclotetrasilane, 32
  - Oligosilanes, 18
    - cyclic, 32
    - linear, 33, 36
  - Oligosilanyl anions, 32–33, 37
  - Oligosilanyl–lithiums, linear, 31–32
  - Organic fluorides, 60
  - Organic halides, 59–60, 74–75
    - adsorption on metal surfaces, 63–65, 73
    - nonsynthetic applications, 69–74
    - physical properties, 60–61
    - reaction with metals, 61–63, 65–69
      - addition of water, 70–71
      - Direct Process Reaction, 67–68, 69, 74–75
      - Grignard reaction, 66–67
  - Organochromium(III) complexes, 160

Organotin trihydrides, 215  
Osmium chloride, as catalyst, 170  
Osmium-phenylethynyl complexes, 125, 136  
Oxidation reactions, alkanes, 169–170

## P

Palladium, 64, 72–73  
Palladium-alkyl complexes, 108  
Palladium-alkynyl complexes, 87, 89, 108, 111  
Palladium(II) catalysts, 170, 171, 182  
Palladium chloride-TPPMS complex, 175  
Palladium(0) complexes, 182  
Palladium-phenylethynyl complexes, 128, 132, 135, 137, 138  
Pentastannanes, 208, 209, 211  
Peralkyl cyclopolystannanes, 218  
Peralkyl distannanes, 195, 197–198, 202  
Peralkylsilyl anions, 11, 12  
Peraryl cyclohexastannanes, 218  
Peraryl distannanes, 194–197, 200  
Permethylpentastannane, 215, 216  
Perstanna-[*n*]-prismanes, 234, 236–237, 239  
Perstanna[1.1.1]propellanes, 235, 236  
1-Phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes, 38  
Phenylethynyl-chromium complexes, 122, 135, 135  
Phenylethynyl-cobalt complexes, 125–126, 137  
Phenylethynyl-gold complexes, 89, 108, 111–113, 119  
Phenylethynyl-hafnium complexes, 122, 135, 136  
Phenylethynyl-iridium complexes, 127–128, 132, 137, 138  
Phenylethynyl-iron complexes, 123–124, 134–136  
Phenylethynyl ligand, 89, 116, 121  
Phenylethynyl-manganese complexes, 123, 136  
Phenylethynyl-metal complexes, 122–138  
Phenylethynyl-molybdenum complexes, 122, 135, 136  
Phenylethynyl-nickel complexes, 128, 135, 137  
Phenylethynyl-osmium complexes, 125, 136  
Phenylethynyl-palladium complexes, 128, 132, 135, 137, 138  
Phenylethynyl-platinum complexes, 128–131, 132, 135, 137, 138  
Phenylethynyl-potassium complexes, 122  
Phenylethynyl-rhodium complexes, 126–127, 134, 135, 137  
Phenylethynyl-ruthenium complexes, 124–125, 136  
Phenylethynyl-tin complexes, 122, 135, 136  
Phenylethynyl-tungsten complexes, 122–123, 134–136  
Phenylethynyl-vanadium complexes, 122, 136  
Phenylethynyl-zinc complexes, 122, 135, 136  
Phenylnonamethylcyclopentasilane, 37–38  
Phenyloligosilanes, action of lithium metal, 31  
Phenylsilyl anions, structure, 7–9  
Phenylsilyl group, 41  
(Phenylsilyl)lithium, 8, 28  
Phosphine, reaction with formaldehyde, 165  
Phosphines, tertiary, *see* Tertiary phosphines  
Phosphinites, 164  
Phosphites, 164  
Phosphorus, reaction with alkyl halides, 72  
Phosphorus-gold bond, 119  
Photoelectron spectroscopy, alkynyl-metal complexes, 83–84  
Platinum, alkylplatinum(III) complexes, 162–163  
Platinum-alkyl complexes, 108  
Platinum-alkynyl complexes, 87–89, 108, 111, 113, 117–118, 139  
Platinum chloride-TPPTS complex, 176–177, 183  
Platinum-chlorine bond, 117–118, 119  
Platinum complexes, catalysis of alkane reactions, 167–170  
Platinum-phenylethynyl complexes, 128–131, 132, 135, 137, 138  
Polycyclic polystannanes  
properties and reactivity, 237–239

- structure, 234–237
- synthesis, 232–234
- Polymerization
  - anionic, masked disilenes, 38–39
  - ring-opening, cyclopenta- and cyclotetrasilanes, 37–38
- Polysilanes, 190, 210, 212
  - cyclic, 37
  - permethylated polycyclic, 33
  - synthesis, 34–37
- Polysilanyl anions, 25–39, 52
- Polysilanylolithiums, 26
- Polystannanes, 189–190
  - branched polystannanes, 215–217
  - cyclopolystannanes, 217–232
  - distannanes, 190–204
  - linear polystannanes, 205–215
  - polycyclic polystannanes, 232–239
  - spectroscopy
    - electronic, 199–202, 210–212
    - NMR, 202–203, 212–214, 216–217, 227–228, 238
    - vibrational, 199–202
- Potassium–phenylethynyl complexes, 122
- [1.1.1]Propellanes, 235, 238
- Propene, hydroformylation, 175–176
- Propionaldehyde, catalytic hydrogenation, 178
- Pulse radiolysis, metal alkyls, 158, 162

## R

- Redox congeners, 115–116
- Rhenium–phenylethynyl complexes, 123, 136
- Rhodium hydrogenation catalysts, enantio-  
meric, 180
- Rhodium–phenylethynyl complexes,  
126–127, 134, 135, 137
- Rhodium–tertiary phosphine complex, 179
- Rhodium–TPPMS complex, 174–178
- Rhodium(III) TPTS complexes, 178
- Rhodium triphenylphosphine, 176
- Ring-opening metathesis polymerization,  
170, 171
- Ring-opening polymerization, cyclopentasi-  
lanes and cyclotetrasilanes, 37–38
- ROMP, *see* Ring-opening metathesis poly-  
merization
- Ruthenium–alkyl complexes, 108
- Ruthenium–alkynyl complexes, 104–105,  
108, 110–111, 114, 117
- Ruthenium–carbon bond, 88–89, 104, 114
- Ruthenium chloride, as catalyst, 170
- Ruthenium–phenylethynyl complexes,  
124–125, 136
- Ruthenium(II)–tertiary phosphine com-  
plex, 179
- Ruthenium–TPPMS complex, 175
- Ruthenium–TPTS complexes, 178

## S

- Schomaker–Stevenson equation, 106
- Semiconductors, 69, 70
- Silacyclopentadienide anions, 22–25
- Sila-enolate, 21–22
- Silicon, Direct Process Reaction, 60,  
67–68, 69, 74–75
- Silicon–alkynyl complexes, 101–102, 104,  
116–117
- Silole, 22
- Siloxysilene, 22
- Silver
  - alkyl halide adsorption on, 64
  - reaction with alkyl halides, 72
- Silyl anions, 1–2, 53
  - alkylsilyl anions, 11–16
  - arylsilyl anions, 3–11
  - definition, 1
  - functionalized, 16–25, 51
  - $\alpha$ -heteroatom-substituted, 17
  - list of, 50–52
  - metal-free, 3
  - NMR data, 7–9, 26–27, 48–49
  - polysilyl anions, 25–39
  - preparation, 2–3
  - synthetic applications, 39–45
  - theoretical study, 45–46
- Silylcadmium, preparation, 3
- Silyl–cobalt compound, 2, 4–5
- Silylcopper, preparation, 3
- Silylcuprate, 3, 31, 40–43
- Silylene, as intermediate in Direct Process  
Reaction, 67–68
- Silylenoids, 47
- Silyllithium, 46–47
  - allyl-bearing, 5
  - optically active, 6
  - polysilane redistribution with, 35

preparation, 2, 4–5  
reaction with chlorosilane, 10–11  
tin-substituted, 31  
Silylmagnesium, preparation, 2, 4–5  
Silylmagnesium reagent, 36–37  
Silylmanganese reagent, 36–37  
Silylmercury, preparation, 3  
Silylmercury compounds, 6, 12  
Silylpotassium, 2, 5, 17  
Silylsodium, 2, 46  
Silylstannanes, 43  
Silylzinc, preparation, 3  
1-Sodio-1-*t*-butyl-2,3,4,5-tetraphenylsila-  
cyclopentadiene, 23  
Sodium 2-bromoethylsulfonate, 164  
Sodium–lead alloy, in preparation of tetra-  
ethyllead, 68–69  
Sodium–tin alloy, 69  
Spectroscopy  
alkynyl–metal complexes, 83–89,  
120–138  
polystannanes, 199–203, 210–214,  
216–217, 227–228, 238  
Stannacyclopentene, 232  
Stannylenes, 232  
Stereochemistry, arylsilylreactions, 10–11  
Supercritical water, 184  
Supramolecular-medium effects, homoge-  
neous catalysis, 181–182

## T

Terminal metal–alkynyl complexes, 90–99,  
103  
Tertiary phosphines, in aqueous solution,  
164–166  
Tertiary phosphine–transition metal com-  
plexes, 166  
chiral, 179–181  
hydroformylation, catalytic, 173–178  
hydrogenation, catalytic, 173–175,  
178–179  
1,1,2,2-Tetraalkyldistannanes, 193  
Tetraalkyllead compounds, 60  
Tetra(*t*-butyl)tin, 192  
Tetraethyllead, industrial synthesis, 68–69  
Tetrakis(trialkylsilyl)disilene, reduction re-  
action, 28  
Tetrakis(trimethylsilyl)silane, 28

Tetralithiosilane, 17  
Tetramethyldiphenyldisilane, 25  
Tetramethyltetraphenylcyclotetrasilanes,  
37  
Tetramethyltin, preparation, 69  
1,1,2,2-Tetraorganodistannanes, 205  
Tetrasilane, 36–37  
Tetrastannanes, 205–211  
Tin–phenylethynyl complexes, 122, 135,  
136  
Tin–sodium alloy, 69  
Tin–tin bond, 203–204, 209–210, 222–223,  
235  
Titanium–alkynyl complexes, 84  
TPPMS, 173  
TPPMS complexes, 174–175  
TPPTS, 163–164, 173–174  
TPPTS complexes, as hydroformylation  
catalysts, 175–178  
TPPTS complexes, as hydrogenation cata-  
lysts, 178–179  
Transition-metal carbonyls, 163–164  
Transition-metal halides, homogeneous ca-  
talysis, 167–171  
Transition metals, alkyl halide complexes,  
62  
Trialkylcalconium ions, 72  
Trialkylgallium, 69  
Trialkylindium, 69  
1,3,5-Triaza-7-phosphaadamantane, 179  
Tri-*tert*-butylsilylsodium anion, 13–14  
Tri(*t*-butyl)tin chloride, 192  
Trichlorohydrosilane, 3  
Trichlorosilane, 21  
Trichlorosilyl anion, 21, 44  
Trichlorosilyllithium, 20–21  
Trimethylaluminum, preparation, 69  
Trimethylsilyl anion, 13–14  
Trimethylsilylethynyl complexes, 101,  
116–117  
Triorgano(*N*-phenylformamido)tins, 205  
Triorganotin hydrides, 205  
Triphenylchlorosilane, 3, 4  
Triphenylphosphine, sulfonation, 164  
Tris(dimethylsilyl)silyllithium, 28  
Tristannanes, 205–211  
Tris(trimethylsilyl)silyllithium, 28  
Trisulfonated triphenylphosphine *see*  
TPPTS  
Tungsten–alkyl complexes, 108

Tungsten-alkynyl complexes, 85, 89, 108, 110, 112, 113

Tungsten-phenylethynyl complexes, 122-123, 134-136

### V

Vanadium-alkynyl complexes, 89, 112, 113

Vanadium-phenylethynyl complexes, 122, 136

Vibrational spectroscopy

alkynyl-metal complexes, 120-139

polystannanes, 199-202

Vitamin B<sub>12</sub>, 161-162

### W

Water

alkyl halide-metal reaction, 70-71

as solvent, 155-156

supercritical water, 184

Water-gas shift reaction, 177

### X

X-ray crystallography, alkynyl-metal complexes, 90-120

### Z

Zinc, reaction with alkyl halides, 73

Zinc-phenylethynyl complexes, 122, 135, 136

Zirconium-alkyl complexes, 108, 109

Zirconium-alkynyl complexes, 108, 109

# ***Cumulative List of Contributors for Volumes 1–36***

- Abel, E. W., **5**, 1; **8**, 117  
 Aguiló, A., **5**, 321  
 Akkerman, O. S., **32**, 147  
 Albano, V. G., **14**, 285  
 Alper, H., **19**, 183  
 Anderson, G. K., **20**, 39; **35**, 1  
 Angelici, R. J., **27**, 51  
 Aradi, A. A., **30**, 189  
 Armitage, D. A., **5**, 1  
 Armor, J. N., **19**, 1  
 Ash, C. E., **27**, 1  
 Ashe III, A. J., **30**, 77  
 Atwell, W. H., **4**, 1  
 Baines, K. M., **25**, 1  
 Barone, R., **26**, 165  
 Bassner, S. L., **28**, 1  
 Behrens, H., **18**, 1  
 Bennett, M. A., **4**, 353  
 Bickelhaupt, F., **32**, 147  
 Birmingham, J., **2**, 365  
 Blinka, T. A., **23**, 193  
 Bockman, T. M., **33**, 51  
 Bogdanović, B., **17**, 105  
 Bottomley, F., **28**, 339  
 Bradley, J. S., **22**, 1  
 Brew, S. A., **35**, 135  
 Brinckman, F. E., **20**, 313  
 Brook, A. G., **7**, 95; **25**, 1  
 Bowser, J. R., **36**, 57  
 Brown, H. C., **11**, 1  
 Brown, T. L., **3**, 365  
 Bruce, M. I., **6**, 273; **10**, 273; **11**, 447; **12**, 379; **22**, 59  
 Brunner, H., **18**, 151  
 Buhro, W. E., **27**, 311  
 Byers, P. K., **34**, 1  
 Cais, M., **8**, 211  
 Calderon, N., **17**, 449  
 Callahan, K. P., **14**, 145  
 Canty, A. J., **34**, 1  
 Cartledge, F. K., **4**, 1  
 Chalk, A. J., **6**, 119  
 Chanon, M., **26**, 165  
 Chatt, J., **12**, 1  
 Chini, P., **14**, 285  
 Chisholm, M. H., **26**, 97; **27**, 311  
 Chiusoli, G. P., **17**, 195  
 Chojinowski, J., **30**, 243  
 Churchill, M. R., **5**, 93  
 Coates, G. E., **9**, 195  
 Collman, J. P., **7**, 53  
 Compton, N. A., **31**, 91  
 Connelly, N. G., **23**, 1; **24**, 87  
 Connolly, J. W., **19**, 123  
 Corey, J. Y., **13**, 139  
 Corriu, R. J. P., **20**, 265  
 Courtney, A., **16**, 241  
 Coutts, R. S. P., **9**, 135  
 Coville, N. J., **36**, 95  
 Coyle, T. D., **10**, 237  
 Crabtree, R. H., **28**, 299  
 Craig, P. J., **11**, 331  
 Csuk, R., **28**, 85  
 Cullen, W. R., **4**, 145  
 Cundy, C. S., **11**, 253  
 Curtis, M. D., **19**, 213  
 Darensbourg, D. J., **21**, 113; **22**, 129  
 Darensbourg, M. Y., **27**, 1  
 Davies, S. G., **30**, 1  
 Deacon, G. B., **25**, 237  
 de Boer, E., **2**, 115  
 Deeming, A. J., **26**, 1  
 Dessy, R. E., **4**, 267  
 Dickson, R. S., **12**, 323  
 Dixneuf, P. H., **29**, 163  
 Eisch, J. J., **16**, 67  
 Ellis, J. E., **31**, 1  
 Emerson, G. F., **1**, 1  
 Epstein, P. S., **19**, 213  
 Erker, G., **24**, 1  
 Ernst, C. R., **10**, 79  
 Errington, R. J., **31**, 91  
 Evans, J., **16**, 319  
 Evans, W. J., **24**, 131  
 Faller, J. W., **16**, 211  
 Farrugia, L. J., **31**, 301



- Faulks, S. J., **25**, 237  
 Fehlner, T. P., **21**, 57; **30**, 189  
 Fessenden, J. S., **18**, 275  
 Fessenden, R. J., **18**, 275  
 Fischer, E. O., **14**, 1  
 Ford, P. C., **28**, 139  
 Forniés, J., **28**, 219  
 Forster, D., **17**, 255  
 Fraser, P. J., **12**, 323  
 Friedrich, H., **36**, 229  
 Friedrich, H. B., **33**, 235  
 Fritz, H. P., **1**, 239  
 Fürstner, A., **28**, 85  
 Furukawa, J., **12**, 83  
 Fuson, R. C., **1**, 221  
 Gallop, M. A., **25**, 121  
 Garrou, P. E., **23**, 95  
 Geiger, W. E., **23**, 1; **24**, 87  
 Geoffroy, G. L., **18**, 207; **24**, 249; **28**, 1  
 Gilman, H., **1**, 89; **4**, 1; **7**, 1  
 Gladfelter, W. L., **18**, 207; **24**, 41  
 Gladysz, J. A., **20**, 1  
 Glänzer, B. I., **28**, 85  
 Green, M. L. H., **2**, 325  
 Grey, R. S., **33**, 125  
 Griffith, W. P., **7**, 211  
 Grovenstein, Jr., E., **16**, 167  
 Gubin, S. P., **10**, 347  
 Guerin, C., **20**, 265  
 Gysling, H., **9**, 361  
 Haiduc, I., **15**, 113  
 Halasa, A. F., **18**, 55  
 Hamilton, D. G., **28**, 299  
 Handwerker, H., **36**, 229  
 Harrod, J. F., **6**, 119  
 Hart, W. P., **21**, 1  
 Hartley, F. H., **15**, 189  
 Hawthorne, M. F., **14**, 145  
 Heck, R. F., **4**, 243  
 Heimbach, P., **8**, 29  
 Helmer, B. J., **23**, 193  
 Henry, P. M., **13**, 363  
 Heppert, J. A., **26**, 97  
 Herberich, G. E., **25**, 199  
 Herrmann, W. A., **20**, 159  
 Hieber, W., **8**, 1  
 Hill, A. F., **36**, 131  
 Hill, E. A., **16**, 131  
 Hoff, C., **19**, 123  
 Hoffmeister, H., **32**, 227  
 Holzmeier, P., **34**, 67  
 Honeyman, R. T., **34**, 1  
 Horwitz, C. P., **23**, 219  
 Hosmane, N. S., **30**, 99  
 Housecroft, C. E., **21**, 57; **33**, 1  
 Huang, Y. Z., **20**, 115  
 Hughes, R. P., **31**, 183  
 Ibers, J. A., **14**, 33  
 Ishikawa, M., **19**, 51  
 Ittel, S. D., **14**, 33  
 Jain, L., **27**, 113  
 Jain, V. K., **27**, 113  
 James, B. R., **17**, 319  
 Janiak, C., **33**, 291  
 Jastrzebski, J. T. B. H., **35**, 241  
 Jenck, J., **32**, 121  
 Jolly, P. W., **8**, 29; **19**, 257  
 Jonas, K., **19**, 97  
 Jones, M. D., **27**, 279  
 Jones, P. R., **15**, 273  
 Jordan, R. F., **32**, 325  
 Jukes, A. E., **12**, 215  
 Jutzi, P., **26**, 217  
 Kaesz, H. D., **3**, 1  
 Kalck, P., **32**, 121; **34**, 219  
 Kaminsky, W., **18**, 99  
 Katz, T. J., **16**, 283  
 Kawabata, N., **12**, 83  
 Kemmitt, R. D. W., **27**, 279  
 Kettle, S. F. A., **10**, 199  
 Kilner, M., **10**, 115  
 Kim, H. P., **27**, 51  
 King, R. B., **2**, 157  
 Kingston, B. M., **11**, 253  
 Kisch, H., **34**, 67  
 Kitching, W., **4**, 267  
 Kochi, J. K., **33**, 51  
 Köster, R., **2**, 257  
 Kreiter, C. G., **26**, 297  
 Krüger, G., **24**, 1  
 Kudaroski, R. A., **22**, 129  
 Kühlein, K., **7**, 241  
 Kuivila, H. G., **1**, 47  
 Kumada, M., **6**, 19; **19**, 51  
 Lappert, M. F., **5**, 225; **9**, 397; **11**, 253;  
     **14**, 345  
 Lawrence, J. P., **17**, 449  
 Le Bozec, H., **29**, 163  
 Lednor, P. W., **14**, 345  
 Linford, L., **32**, 1

- Longoni, G., **14**, 285  
 Luijten, J. G. A., **3**, 397  
 Lukehart, C. M., **25**, 45  
 Lupin, M. S., **8**, 211  
 McGlinchey, M. J., **34**, 285  
 McKillop, A., **11**, 147  
 McNally, J. P., **30**, 1  
 Macomber, D. W., **21**, 1; **25**, 317  
 Maddox, M. L., **3**, 1  
 Maguire, J. A., **30**, 99  
 Maitlis, P. M., **4**, 95  
 Mann, B. E., **12**, 135; **28**, 397  
 Manuel, T. A., **3**, 181  
 Markies, P. R., **32**, 147  
 Mason, R., **5**, 93  
 Masters, C., **17**, 61  
 Matsumura, Y., **14**, 187  
 Mayr, A., **32**, 227  
 Meister, G., **35**, 41  
 Mingos, D. M. P., **15**, 1  
 Mochel, V. D., **18**, 55  
 Moedritzer, K., **6**, 171  
 Molloy, K. C., **33**, 171  
 Monteil, F., **34**, 219  
 Morgan, G. L., **9**, 195  
 Morrison, J. A., **35**, 211  
 Moss, J. R., **33**, 235  
 Mrowca, J. J., **7**, 157  
 Müller, G., **24**, 1  
 Mynott, R., **19**, 257  
 Nagy, P. L. I., **2**, 325  
 Nakamura, A., **14**, 245  
 Nesmeyanov, A. N., **10**, 1  
 Neumann, W. P., **7**, 241  
 Norman, N. C., **31**, 91  
 Ofstead, E. A., **17**, 449  
 Ohst, H., **25**, 199  
 Okawara, R., **5**, 137; **14**, 187  
 Oliver, J. P., **8**, 167; **15**, 235; **16**, 111  
 Onak, T., **3**, 263  
 Oosthuizen, H. E., **22**, 209  
 Otsuka, S., **14**, 245  
 Pain, G. N., **25**, 237  
 Parshall, G. W., **7**, 157  
 Paul, I., **10**, 199  
 Peres, Y., **32**, 121  
 Petrosyan, W. S., **14**, 63  
 Pettit, R., **1**, 1  
 Pez, G. P., **19**, 1  
 Poland, J. S., **9**, 397  
 Poliakoff, M., **25**, 277  
 Popa, V., **15**, 113  
 Pourreau, D. B., **24**, 249  
 Powell, P., **26**, 125  
 Pratt, J. M., **11**, 331  
 Prokai, B., **5**, 225  
 Pruett, R. L., **17**, 1  
 Rao, G. S., **27**, 113  
 Raubenheimer, H. G., **32**, 1  
 Rausch, M. D., **21**, 1; **25**, 317  
 Reetz, M. T., **16**, 33  
 Reutov, O. A., **14**, 63  
 Rijkens, F., **3**, 397  
 Ritter, J. J., **10**, 237  
 Rochow, E. G., **9**, 1  
 Rokicki, A., **28**, 139  
 Roper, W. R., **7**, 53; **25**, 121  
 Roundhill, D. M., **13**, 273  
 Rubezhov, A. Z., **10**, 347  
 Salerno, G., **17**, 195  
 Salter, I. D., **29**, 249  
 Satgé, J., **21**, 241  
 Schade, C., **27**, 169  
 Schaverien, C. J., **36**, 283  
 Schmidbaur, H., **9**, 259; **14**, 205  
 Schrauzer, G. N., **2**, 1  
 Schubert, U., **30**, 151  
 Schulz, D. N., **18**, 55  
 Schumann, H., **33**, 291  
 Schwabke, G. L., **1**, 89  
 Seppelt, K., **34**, 207  
 Setzer, W. N., **24**, 353  
 Seyferth, D., **14**, 97  
 Shapakin, S. Yu., **34**, 149  
 Shen, Y. C., **20**, 115  
 Shriver, D. F., **23**, 219  
 Siebert, W., **18**, 301; **35**, 187  
 Sikora, D. J., **25**, 317  
 Silverthorn, W. E., **13**, 47  
 Singleton, E., **22**, 209  
 Sinn, H., **18**, 99  
 Skinner, H. A., **2**, 49  
 Slocum, D. W., **10**, 79  
 Smallridge, A. J., **30**, 1  
 Smeets, W. J. J., **32**, 147  
 Smith, J. D., **13**, 453  
 Speier, J. L., **17**, 407  
 Spek, A. L., **32**, 147  
 Stafford, S. L., **3**, 1  
 Stańczyk, W., **30**, 243

- Stone, F. G. A., **1**, 143; **31**, 53; **35**, 135  
Su, A. C. L., **17**, 269  
Suslick, K. M., **25**, 73  
Süss-Fink, G., **35**, 41  
Sutin, L., **28**, 339  
Swincer, A. G., **22**, 59  
Tamao, K., **6**, 19  
Tate, D. P., **18**, 55  
Taylor, E. C., **11**, 147  
Templeton, J. L., **29**, 1  
Thayer, J. S., **5**, 169; **13**, 1; **20**, 313  
Theodosiou, I., **26**, 165  
Timms, P. L., **15**, 53  
Todd, L. J., **8**, 87  
Touchard, D., **29**, 163  
Traven, V. F., **34**, 149  
Treichel, P. M., **1**, 143; **11**, 21  
Tsuji, J., **17**, 141  
Tsutsui, M., **9**, 361; **16**, 241  
Turney, T. W., **15**, 53  
Tyfield, S. P., **8**, 117  
Usón, R., **28**, 219  
Vahrenkamp, H., **22**, 169  
van der Kerk, G. J. M., **3**, 397  
van Koten, G., **21**, 151; **35**, 241  
Veith, M., **31**, 269  
Vezey, P. N., **15**, 189  
von Ragué Schleyer, P., **24**, 353; **27**, 169  
Vrieze, K., **21**, 151  
Wada, M., **5**, 137  
Walton, D. R. M., **13**, 453  
Wailles, P. C., **9**, 135  
Webster, D. E., **15**, 147  
Weitz, E., **25**, 277  
West, T., **5**, 169; **16**, 1; **23**, 193  
Werner, H., **19**, 155  
White, D., **36**, 95  
Wiberg, N., **23**, 131; **24**, 179  
Wiles, D. R., **11**, 207  
Wilke, G., **8**, 29  
Williams, R. E., **36**, 1  
Winter, M. J., **29**, 101  
Wojcicki, A., **11**, 87; **12**, 31  
Yamamoto, A., **34**, 111  
Yashina, N. S., **14**, 63  
Ziegler, K., **6**, 1  
Zuckerman, J. J., **9**, 21  
Zybill, C., **36**, 229

# Cumulative Index

## Volumes 37 and 38

	VOL.	PAGE
Andersen, Jo-Ann M., and Moss, John R., <i>Alkyl(pentacarbonyl) Compounds of the Manganese Group Revisited</i> .....	37	169
Carty, Arthur J., <i>see</i> Doherty, Simon		
Corrigan, John F., <i>see</i> Doherty, Simon		
Doherty, Simon, Corrigan, John F., Carty, Arthur J., and Sappa, Enrico, <i>Homometallic and Heterometallic Transition Metal Allenyl Complexes: Synthesis, Structure, and Reactivity</i> .....	37	39
Hopkins, Michael D., <i>see</i> Manna, Joseph		
John, Kevin D., <i>see</i> Manna, Joseph		
Kawachi, Atsushi, <i>see</i> Tamao, Kohei		
Lotz, Simon, Van Rooyen, Petrus H., and Meyer, Rita, $\sigma$ , $\pi$ -Bridging Ligands in Bimetallic and Trimetallic Complexes .....	37	219
Manna, Joseph, John, Kevin D., and Hopkins, Michael D., <i>The Bonding of Metal-Alkynyl Complexes</i> .....	38	79
Manners, Ian, <i>Ring-Opening Polymerization of Metallocenophanes: A New Route to Transition Metal-Based Polymers</i> .....	37	131
Meyer, Rita, <i>see</i> Lotz, Simon		
Moss, John R., <i>see</i> Andersen, Jo-Ann M.		
Roundhill, D. M., <i>Organotransition-Metal Chemistry and Homogeneous Catalysis in Aqueous Solution</i> .....	38	155
Sakurai, Hideki, <i>see</i> Sekiguchi, Akira		
Sappa, Enrico, <i>see</i> Doherty, Simon		
Sekiguchi, Akira, and Sakurai, Hideki, <i>Cage and Cluster Compounds of Silicon, Germanium, and Tin</i> .....	37	1
Sita, Lawrence R., <i>Structure/Property Relationships of Polystyranes</i> .....	38	189
Tamao, Kohei, Kawachi, Atsushi, <i>Silyl Anions</i> .....	38	1
Thayer, John S., <i>Not for Synthesis Only: The Reactions of Organic Halides with Metal Surfaces</i> .....	38	59
Van Rooyen, Petrus H., <i>see</i> Lotz, Simon		

ISBN 0-12-031138-0



9 780120311385

90065